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An experimental setup for methanol production for renewable energy storage

Diplomityö, joka on jätetty opinnäytteenä tarkastettavaksi diplomi-insinöörin tutkintoa varten.

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Diplomityön tiivistelmä

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Työn nimi Kokeellinen laitteisto metanolin tuotannolle uusiutuvan energian varastointiin

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Tiivistelmä

Ilmastonmuutoksen mukanaan tuomat haasteet vaativat laajan kirjon uusia ratkaisuja kansainvälisten hiilineutraalisuustavoitteiden saavuttamiseksi. Power-to-X teknologioilla (P2X) tulee olemaan merkittävä rooli näiden tavoitteiden saavuttamisessa. P2X:llä tarkoitetaan sähköenergian muuntamista jonkin yhdisteen kemialliseksi energiaksi, josta energia voidaan myöhemmin hyödyntää.

Metanolin tuotanto hiilidioksidista ja vedystä metanolisynteesin avulla mahdollistaa uusiutuvalla energialla tuotetun sähkön varastoimisen metanoliin, jota voidaan käyttää myöhemmin esimerkiksi polttoaineena. Prosessista on mahdollista tehdä täysin hiilineutraali, mikäli prosessiin tarvittava vety tuotetaan vedestä elektrolyysin avulla, ja hiilidioksidi otetaan talteen teollisuuden savukaasuista, tai suoraan ilmasta.

Tämä diplomityö keskittyy metanolisynteesiin hiilidioksidista ja vedystä. Diplomityöhön sisältyy kokeellisen metanolireaktorilaitteiston rakentamisen suunnittelu ja toteutus. Koelaitteiston kokoonpano ja rakenne esitellään diplomityössä. Työssä tutustutaan CO_2 -pohjaisen metanolisynteesin toimintaperiaatteisiin, ja metanolisynteesin kemiallisen tasapainon laskemiseen kehitetään yksinkertaistettu malli, jonka avulla voidaan arvioida hiilidioksidin suurinta mahdollista konversiota metanoliksi. Diplomityössä tehdään myös kirjallisuuskatsaus muiden aiemmin tekemiin, tässä työssä luodun koelaitteiston kanssa samankaltaisilla laitteistoilla tehtyihin kokeellisiin tutkimuksiin aiheesta.

Kirjallisuuskatsauksessa tarkastelluissa kokeellisissa tutkimuksissa suurin saavutettu konversio oli alle 18% tyypillisissä reaktio-olosuhteissa (250 °C, 50 bar), kun syöttökaasun kokoonpano oli stoikiometrinen. Työssä kehitetyn mallin mukaan näissä olosuhteissa konversio hiilidioksidista metanoliksi on tasapainotilanteessa noin 20%. Kierrättämällä reagoimattomia kaasuja takaisin reaktoriin kokonaiskonversiota voitaisiin kasvattaa. CO_2 -pohjaisella metanolisynteesillä on kuitenkin selkeitä etuja perinteiseen synteesikaasuun perustuvaan metanolisynteesiin nähden, merkittävimpänä vähäinen sivutuotteiden muodostuminen metanolisynteesissä, sekä mahdollisuus tehdä prosessista hiilineutraali.

Avainsanat Metanoli, Metanolisynteesi, Koelaitteisto, P2X, Kemiallinen tasapaino, Hiilidioksidi, Vety, CO_2, H_2.

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Abstract of master's thesis

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Abstract

The challenges posed by climate change require a broad spectrum of new solutions in meeting the international goals for carbon neutrality. Power-to-X technologies (P2X) will play a major role in reaching these goals. P2X means the process of converting electrical energy into chemical energy of some compound, where the energy can be later discharged when needed.

Methanol production from carbon dioxide and hydrogen via methanol synthesis allows the storage of renewable electricity to methanol, that can be later used as a fuel for example. This process can be designed to be completely carbon neutral, if the hydrogen needed for the process is produced via water electrolysis, and if the carbon dioxide needed for the process is captured from industrial flue gases or directly from air.

This master's thesis focuses on methanol synthesis from carbon dioxide and hydrogen. Planning and construction of an experimental methanol reactor setup for CO2-based methanol synthesis is included in this thesis. The structure of the experimental setup with the equipment involved is presented in this master's thesis. In this thesis we explore the working principles of CO2-based methanol synthesis. A simple model to estimate the equilibrium conversion of CO2 to methanol is developed in this thesis. A literature review is conducted concerning other experimental studies about methanol synthesis from CO2 and H2 with similar experimental setups as the one constructed in this master's thesis.

The highest single-pass conversion of CO2 to methanol achieved among the studies in the literature review was below 18% in typical reaction conditions (250 °C, 50 bar) when the feed gas composition was stoichiometric. According to the equilibrium model developed in this thesis, the equilibrium conversion from CO2 to methanol is around 20 % at these conditions. By including re-circulation of unreacted gases back to the reactor, the overall conversion could be increased. Nevertheless, CO2-based methanol production has clear benefits over traditional syngas-based methanol synthesis, the most notable ones being the lower by-product formation and the possibility to make the process completely carbon neutral.

Keywords Methanol, Methanol synthesis, Experimental setup, P2X, Chemical equilibrium, Carbon dioxide, Hydrogen, CO2, H2.

Foreword

This master's thesis serves as a start of an experimental P2X project carried out in Aalto University's School of Engineering. The experimental setup presented in this thesis was designed and constructed in co-operation with other members of the Energy Conversion research group in Aalto University. This experimental setup will be used in P2X research for studying methanol production from carbon dioxide and hydrogen.

I want to thank Annukka Santasalo-Aarnio, for providing me this opportunity to challenge myself and learn about this extremely interesting topic, and to work with amazing co-workers. I thank my advisor, Judit Nyari, for the wonderful support she has provided throughout this process. I am especially grateful to Mika Ahlgren and Kari Saari for making this all possible with their work and dedication to our experimental setup.

I would like to thank my parents, Saara and Kari, and my little brother Ville, for their endless support and encouragement during my university studies. Especially, I want to thank my girlfriend Miia for sharing most of this journey with me and giving me her love and support. I also want to thank my friends for the moments we got to experience together. Finally, I want to thank the Finnish education system for securing access to high-quality education for me and others.

Espoo, 24.7.2020

Markus Laitinen

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List of abbreviations

CCS – CO_2 capture and storage

CRI – Carbon Recycling International

DME – Dimethyl ether

FID – Flame ionization detector

GC – Gas chromatography

GHSV – Gas hourly space velocity

KOH – Potassium hydroxide

MeOH – Methanol

MTBE – Methyl tert-butyl ether

NIRE – National Institute for Resources and Environment

PEM - Polymer electrolyte membranes

P2X – Power-to-X

RITE – Research Institute of Innovative Technology for the Earth

RWGS – Reverse water-gas shift (reaction)

SOEC – solid oxide electrolysis cell

STY – Space time yield

TCD – Thermal conductivity detector

1 Introduction

In order to mitigate climate change, many countries have committed to reduce their CO_2 emissions. In the 2015 Paris agreement, with close to 190 parties including EU and its member states, a major part of the world agreed on a common goal of limiting the global warming to 2 °C (European Commission, n.d.a). In addition, the European Commission has set their own targets of having 40% less greenhouse gas emissions in 2030 compared to 1990 levels (European Commission, n.d.b), and a long-term strategy of being climate-neutral in 2050 (European Commission, n.d.c). Reducing the use of fossil fuels in energy production plays a major role in achieving these goals. This requires a large-scale shift from fossil fuels to carbon neutral energy, and this shift poses a list of challenges to overcome. The challenges of replacing fossil fuels with clean energy sources emerge in electricity, heat, and fuel production.

In electricity production, renewable electricity sources such as solar and wind are promising for their abundancy. However, one of the biggest challenges in their large-scale implementation is that they are intermittent in their availability. Therefore, the electricity production with these technologies is also intermittent, and thus not in human control. If the electricity system was too heavily based on solar and wind without any means to store the energy, there would be an oversupply of cheap electricity during peak hours of sunlight or wind, and there would not be enough electricity available during calm and cloudy weather.

Storing the electricity produced by solar and wind, is a crucial step towards reaching these climate goals. There are already many technologies available to store this electricity. However, while providing many benefits, many of these technologies such as batteries and pumped hydro, have a limited capacity for storing energy. After a certain amount of energy is stored into a battery, it can no longer store more energy before a portion of it has been discharged. (Argyrou et al., 2018)

Power-to-X (P2X) is the concept of using electricity to create some gas, liquid or other product that can be used as an energy storage. This means converting electrical energy into chemical energy of a fuel (Vázquez et al., 2018). This allows us to convert the excess electricity produced by intermittent renewables, such as solar and wind, to something useful, such as a fuel. P2X technologies do not usually have similar limitations of storage capacity as batteries. Although the fuel produced with P2X needs to be stored, it is much simpler to scale up and increase the capacity of a fuel storage than the capacity of a battery, especially when the fuel is liquid.

The shift from fossil fuels to green energy sources also poses challenges to fuel production. According to the IEA report World Energy Outlook 2004 (IEA, 2004) the share of oil in transport energy demand has been around 95% from 1971 (to 2004) and will remain in their projections at approximately that level at least until 2030. In 2019 petroleum products still accounted for about 91% of the U.S. total energy sources in transportation sector (EIA, 2020).

The main alternatives for petroleum-based fuels in transportation are biofuels and synthetic fuels. The problem with biofuels is that its production volumes cannot reach high enough to replace fossil fuels with the limited land area available to produce the biofuels. Synthetic fuels produced via P2X technologies can be a part of the solution to this challenge. The synthetic fuel considered in this master's thesis as a P2X product is methanol, which can be

produced from hydrogen and carbon dioxide. So, first by using electricity to produce hydrogen, and then by using that hydrogen together with carbon dioxide to generate methanol.

This master's thesis studies the methanol production from carbon dioxide and hydrogen via methanol synthesis. This thesis attempts to answer the following research questions: How does methanol synthesis from CO_2 and H_2 work? How does methanol production from CO_2 and H_2 compare to conventional methanol production? These questions are answered in chapters 2 and 3 of this thesis. The following research questions are addressed in chapter 4: What experimental studies have been conducted on CO_2 hydrogenation to methanol and how? What has been the methanol production scale and equipment used in these studies, and what results have they got? In chapter 5 we present our own experimental reactor for methanol production from CO_2 and H_2 answering the last research question: How to design and construct an experimental reactor setup for methanol production from CO_2 and H_2?

2 Methanol

2.1 Methanol as an energy carrier

Methanol, also known as methyl alcohol, (CH_3OH, also expressed as MeOH), is the simplest alcohol with only one carbon atom. Methanol is a widely used material in many applications. Most of the methanol produced worldwide is used as a raw material in chemical industry. Formaldehyde, methyl tert-butyl ether (MTBE) and acetic acid are the most common products derived from methanol covering together about 2/3 of the global methanol demand (Dalena et al., 2018). The different uses of methanol are displayed in Figure 1. According to Figure 1, only 8 % of methanol produced globally is being used as a fuel (Dalena et al., 2018). However, this 8 % fuel usage considers only direct usage of methanol as a fuel. In addition to that 8 % of direct use, methanol can be used as raw material for products that are used in fuel applications. For example, MTBE is used as a blending component of gasoline. Methanol Institute, a global trade association for methanol, estimates that energy applications currently account for 40 % of the total methanol consumption (Methanol institute, n.d.).

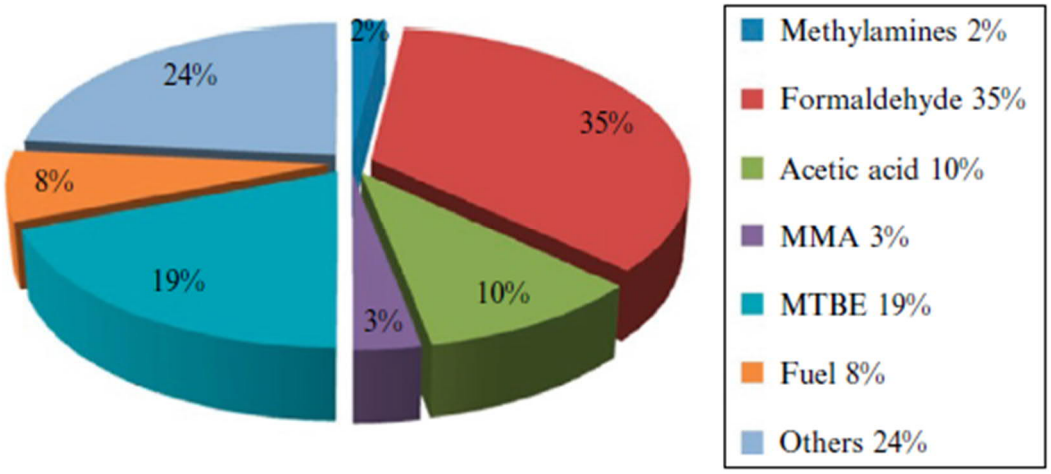


Figure 1. Different uses of methanol produced globally (Dalena et al., 2018). MMA stands for methyl methacrylate.

Although methanol has many uses in the chemical industry, this master's thesis focuses mostly on the potential of methanol as an energy carrier for renewable energy. However, it is important to point out the huge importance of methanol in the chemical industry. Figure 2 presents some of the products and end uses for methanol.

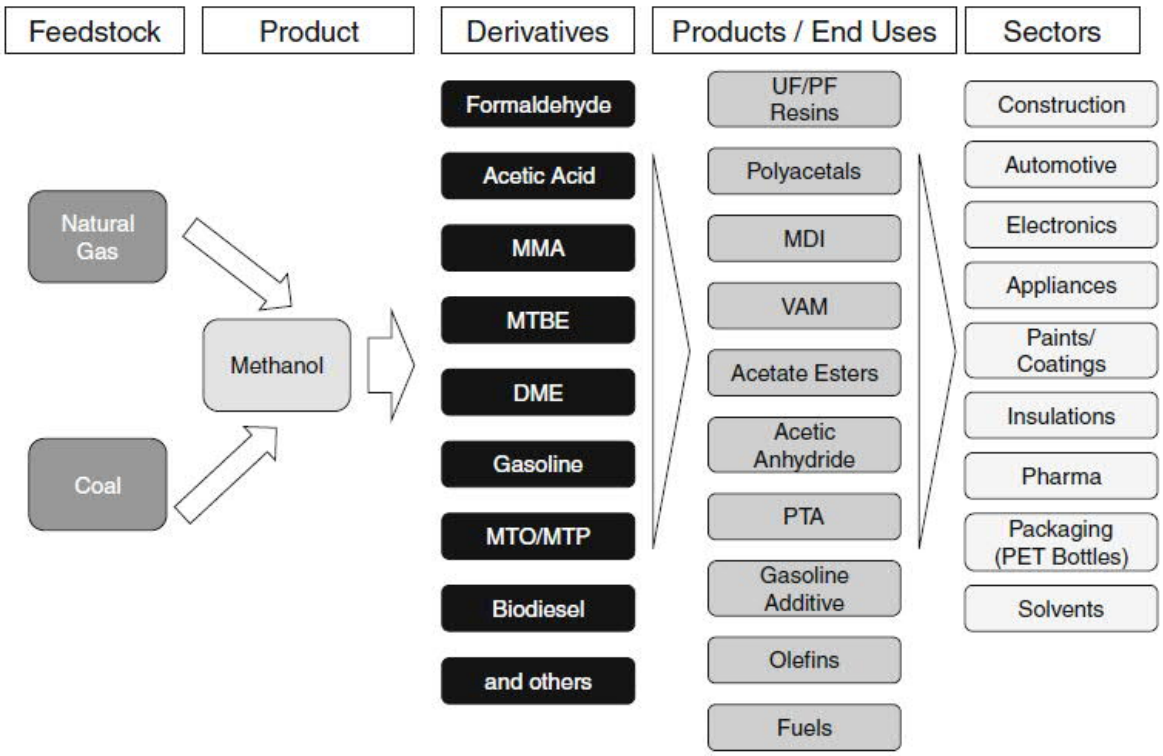


Figure 2. Different end uses of methanol (Bertau et al. et al., 2014).

As discussed in the introduction, renewable energy sources such as solar and wind are intermittent in their nature, and as such produce large amounts of excess electricity at times. This excess electricity generation during peak hours poses many problems to the energy system and the grid. P2X technologies can provide a solution to this, as they can be implemented to convert this excess electricity to something useful. The excess electricity can be used in the production of some chemical in which the energy can be stored. This chemical can be hydrogen, methane, methanol, or something else. In the process examined in this master's thesis, that chemical is hydrogen, which is then converted to methanol via methanol synthesis with carbon dioxide. Methanol production from CO_2 and H_2 can be seen simultaneously as a carbon dioxide storage and a renewable energy storage method. Different P2X technologies, that also serve as CO_2 storage, are presented in Figure 3 by Bailera et al. (2017).

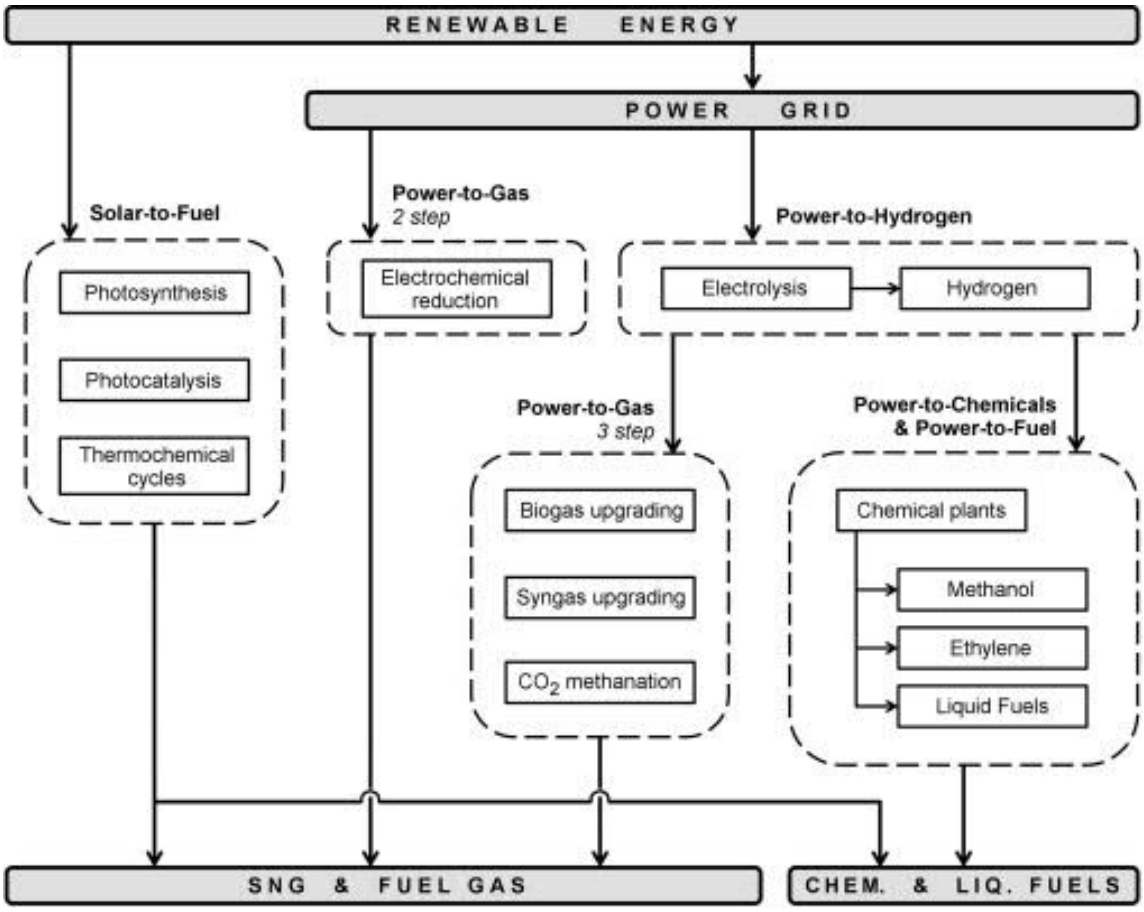


Figure 3. Different technologies for simultaneous storage of renewable energy and carbon dioxide presented by Bailera et al. (2017).

The use of methanol as renewable energy storage material involves many steps. First, excess electricity needs to be converted into chemical energy of methanol. Then, the methanol produced needs to be stored and transported. Finally, the methanol needs to be used as a fuel to discharge the energy when needed. For methanol to be considered a feasible energy storage option, and a good energy carrier, the implementation of each of these steps in the case of methanol needs to be practically reasonable.

One of the most important qualities for a good energy carrier, or a fuel, is that it has a high energy density. Higher energy density allows more energy to be stored in the same amount of the storage material. Energy density of a storage material can be expressed as gravimetric energy density (stored energy per unit of mass) or volumetric energy density (stored energy per unit of volume).

Lehtonen (2019) made a great illustration in his master's thesis about the relative gravimetric energy densities of the different compounds that each play a key role in the methanol production today. The illustration is presented in Figure 4. Among these molecules are the most common raw materials of methanol: carbon C (or coal) and methane CH_4 (or natural gas), and the components of synthesis gas-based methanol production: carbon monoxide CO, carbon dioxide CO_2, hydrogen H_2 and methanol itself CH_3OH. Methanol production processes are explained in more detail in chapters 2.2 and 2.3.

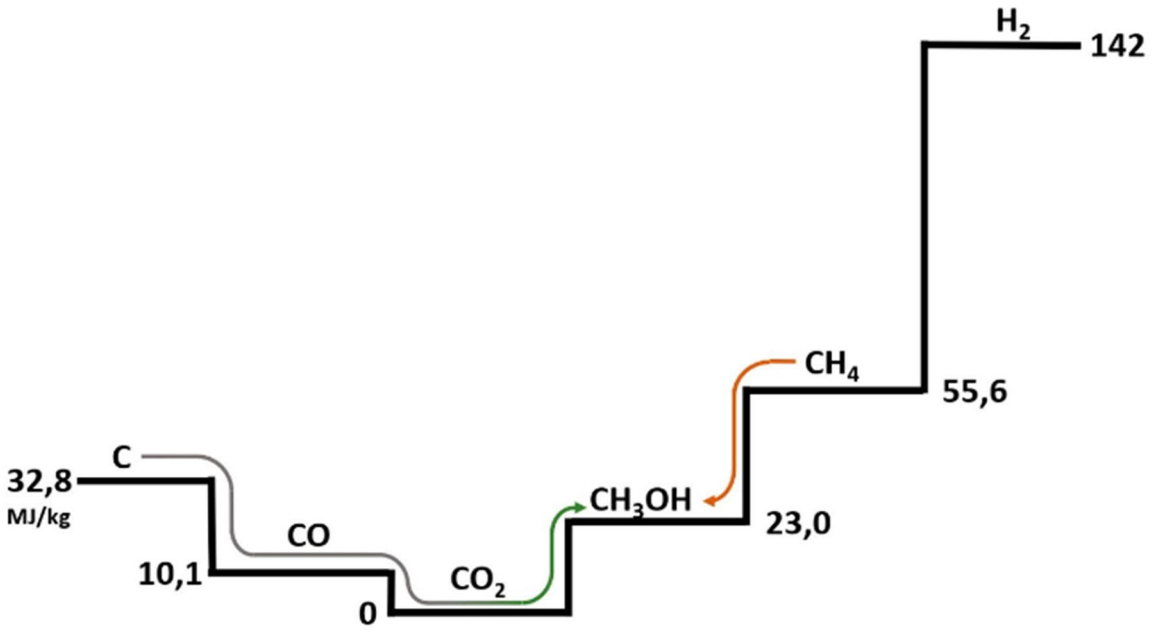


Figure 4. Gravimetric energy densities of different materials (Lehtonen, 2019).

This master's thesis topic focuses on methanol production from CO_2 and H_2 via methanol synthesis. This means that the chemical energy of hydrogen is converted into the chemical energy of methanol by making it react with carbon dioxide. As seen from Figure 4, H_2 has over six times higher gravimetric energy density than MeOH. On a quick note it might seem as if 5/6 of the energy contained in H_2 is lost in the conversion to MeOH. However, this is not the case since 1 kg of H_2 does not convert into 1 kg of MeOH. In the methanol synthesis 3 mol of H_2 required to produce 1 mol of MeOH (methanol production from CO_2 is described in more detail in chapter 2.3). The molar masses of H_2 and MeOH are 2.016 g/mol and 32.04 g/mol respectively (Engineering ToolBox, 2009), so only less than 190 g of H_2 is consumed in the production of 1 kg of MeOH. This together with the gravimetric energy densities presented in Figure 4, means that methanol contains 85.8 % of the energy content of its raw materials (H_2 and CO_2).

This does not take away the fact that the gravimetric energy density of MeOH is much lower than that of H_2. To store the same amount of energy, a higher amount of mass is required if the energy carrier is MeOH than if it is H_2. So, the MeOH storage will be heavier than the H_2 storage, which is not desirable. However, methanol is liquid in ambient conditions, while hydrogen is gaseous. This gives MeOH significantly better volumetric energy density compared to H_2. The same materials from Figure 4 are being compared by their volumetric energy densities in standard conditions (0 °C, 1 bar) in Figure 5. Keep in mind that the scale in Figure 5 is logarithmic.

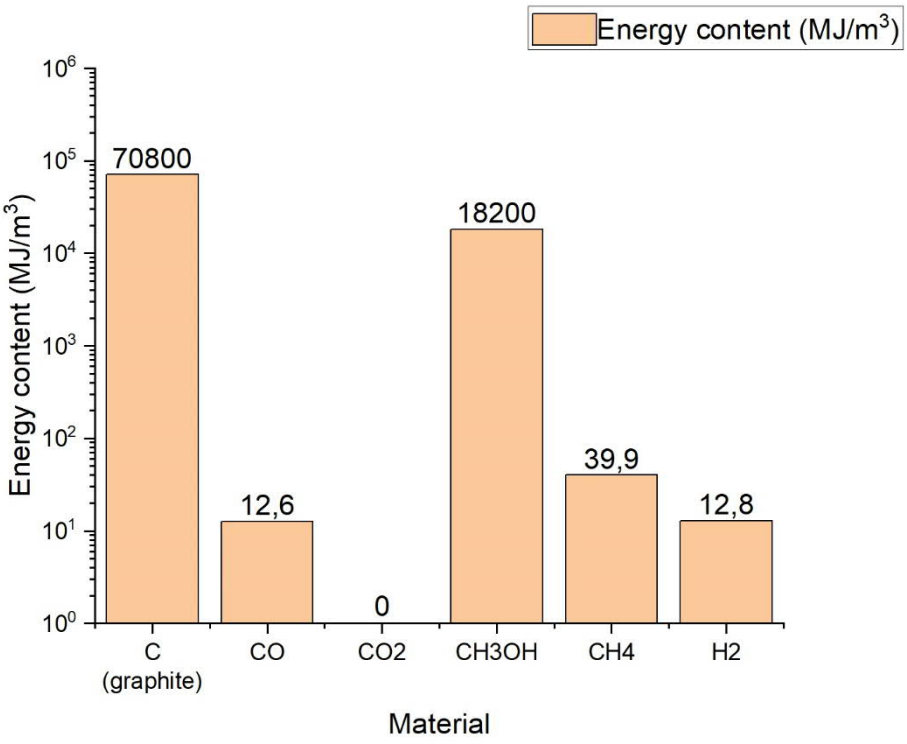


Figure 5. Volumetric energy densities of different materials on a logarithmic scale for comparison to Figure 4. (Values from: Engineering ToolBox, 2003a; Engineering ToolBox, 2003b; Mindat, n.d.)

High volumetric energy density of the fuel is very important especially in vehicles where volume needs to be restricted. This is one of the clear advantages of methanol over H_2, and makes the conversion from H_2 to MeOH reasonable.

However, this comparison presented in Figure 5 can be somewhat misleading, because the hydrogen is not stored in standard conditions, but is pressurized. Fuel cell cars that use H_2 as an energy source typically store it in high pressures. The internationally agreed standard pressure for gaseous H_2 storage in automotive systems is 70 MPa, or 700 bar (Dagdougui et al., 2018). Therefore, it is more reasonable to compare the volumetric energy densities of MeOH and pressurized H_2. But even when pressurized to 700 bar, hydrogen does not come close to the volumetric energy density of methanol (U.S. Department of Energy, n.d.). Figure 6 presents some common energy carriers in terms of their gravimetric and volumetric energy densities, including pressurized H_2 at 350 bar and 700 bar.

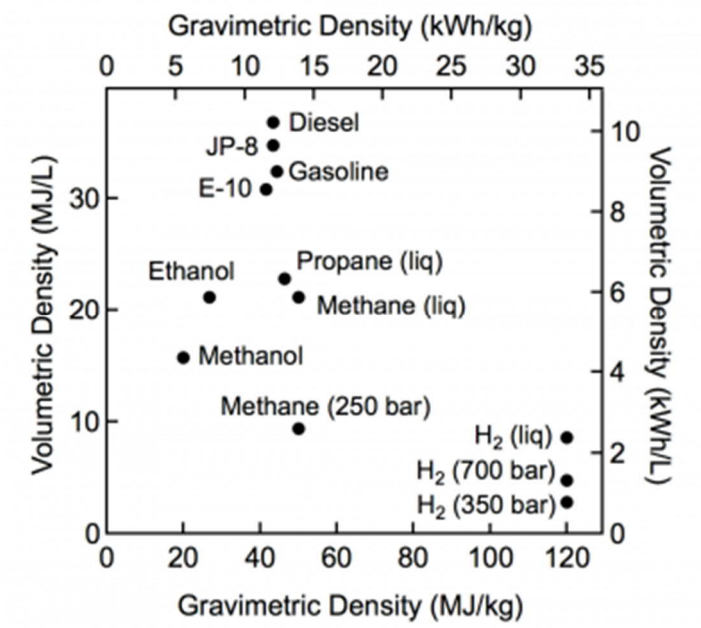


Figure 6. Volumetric and gravimetric energy densities of different fuels. Source: U.S. Department of Energy, n.d.

In addition to having high energy density, a good energy carrier also needs to be easily stored and transported. Methanol is liquid at ambient conditions, and has a boiling point of 64.6 °C and a freezing point of -97.6 °C. These properties allow MeOH to be distributed in pipelines and easily transported in big tankers. Being liquid, methanol is easy to store. Compared to gaseous H_2, MeOH can be stored efficiently in ambient pressure. (Bertau et al., 2014)

Finally, from a good energy carrier the energy needs to be discharged easily and used in relevant applications. Methanol provides countless options for its use in energy sector. Methanol can be used in gasoline engines either directly or it can be converted into MTBE. MeOH is often used as a blending compound with gasoline, such as M15 having 15 % of MeOH in gasoline, or M85 having 85% (Bertau et al., 2014). MeOH can be converted to DME (dimethyl ether) by dehydration of methanol, and this DME can be used in diesel engines as a substitute for diesel with an octane number of 55 (Bertau et al., 2014). Also, MeOH can be used as a fuel in fuel cell vehicles with an electric motor in either direct methanol fuel cell or as a hydrogen carrier in reformed methanol fuel cells (Bertau et al., 2014).

Compared to gasoline and diesel, methanol burns cleaner as it combusts into CO_2 and water. Therefore, methanol combustion does not produce nitrogen oxides or particulate matter emissions. However, incomplete combustion of methanol can produce gaseous pollutants such as formaldehyde and unreacted methanol. (Bertau et al., 2014) Methanol is also less dangerous than crude oil as it blends with water and is biodegradable. Methanol does not persist in the environment, so a possible MeOH spill would not be as harmful as an oil spill. (Bertau et al., 2014)

Methanol has much potential in energy storage applications and as a fuel. Storing and transporting methanol is easy, because it is liquid at ambient conditions. This makes it an attractive candidate as an alternative renewable fuel.

2.2 Conventional methanol production

In conventional methanol production, methanol is produced from synthesis gas, also known as syngas. Syngas is a gas mixture that consists mainly of carbon monoxide (CO) and hydrogen (H_2), but it often contains some carbon dioxide (CO_2) as well. The process of conventional methanol production involves three steps (Biedermann et al., 2006):

1. Synthesis gas production
2. Methanol synthesis
3. Methanol distillation

The first step in conventional methanol production is the production of synthesis gas. Syngas can be produced from a variety of fossil fuel sources such as coal, lignite, natural gas, shale gas, oil and refinery residues, as well as from non-fossil sources such as biomass (Bertau et al., 2014). However, syngas is almost exclusively produced from natural gas, except in China where a large amount of the production facilities use coal as the hydrocarbon source for syngas (Methanol Market Services Asia, n.d.).

Syngas is generated from natural gas (CH_4) most commonly via a process called steam reforming. Before the steam reforming process sulfur-containing compounds must be removed from the natural gas. In steam reforming the hydrocarbons, CH_4 in this case, are made to react with steam (H_2O) and converted into a gas mixture containing H_2, CO and CO_2. The chemical reaction for steam reforming is presented in Equation 2.1 (Bertau et al., 2014).

$$CH_4 + H_2O \leftrightarrows CO + 3H_2, \qquad \Delta_r H^\circ = 206\ \frac{kJ}{mol} \tag{2.1}$$

Steam reforming of natural gas is strongly endothermic with the reaction presented in Equation 2.1 having a reaction enthalpy of 206 $\frac{kJ}{mol}$. So, to achieve high conversion the process requires high temperatures and low pressures (Biedermann et al., 2006). Typical product gas exit temperatures for the steam reforming process are between 700 and 900 °C. Synthesis gas generation is the most expensive step in the conventional methanol production process (Biedermann et al., 2006).

The proportions of CO, H_2 and CO_2 in the syngas can vary between different syngas mixtures based mostly on the production method and end use of the gas. A stoichiometric number S is used to characterize the composition of syngas. It is defined with the molar ratios of H_2, CO_2 and CO according to Equation 2.2. The syngas produced by steam reforming of natural gas has the S value of 3. For methanol synthesis the ideal value of S for the syngas is 2. (Bozzano & Manenti, 2016)

$$S = \frac{moles(H_2) - moles(CO_2)}{moles(CO_2) + moles(CO)} \tag{2.2}$$

The second step in conventional methanol production is the methanol synthesis, where raw MeOH is produced from syngas. Methanol synthesis is carried out in elevated temperatures and pressures in the presence of a catalyst in a reactor. There are three reactions that take place in methanol synthesis: carbon dioxide hydrogenation (Equation 2.3), carbon monoxide

hydrogenation (Equation 2.4) and reverse water-gas shift reaction (RWGS) (Equation 2.5). These reactions are presented below. (Bertau et al., 2014)

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O, \qquad \Delta_r H^\circ(298\ K) = -49{,}4\frac{kJ}{mol} \tag{2.3}$$

$$CO + 2H_2 \leftrightarrows CH_3OH, \qquad \Delta_r H^\circ(298\ K) = -90{,}5\frac{kJ}{mol} \tag{2.4}$$

$$CO_2 + H_2 \leftrightarrows CO + H_2O, \qquad \Delta_r H^\circ(298\ K) = 41{,}1\frac{kJ}{mol} \tag{2.5}$$

These reactions take place on the surface of the catalyst inside the reactor. All three of these reactions (Eqs. 2.3 – 2.5) are present both in conventional methanol synthesis and in methanol synthesis from CO_2 and H_2 (see chapter 2.3). The $\Delta_r H^\circ$ values present the reaction enthalpies for Eqs. 2.3 – 2.5 in the forward direction (Portha et al., 2017). These reaction enthalpies depend on the temperature and pressure inside the reactor, and therefore they are often given in standard conditions. Standard temperature and pressure (STP) are defined as 0 °C and 1 bar (absolute pressure) (IUPAC, 1997), but for reaction enthalpies the temperature of 25 °C (298 K) is often used. These $\Delta_r H^\circ$ values given by Portha et al. (2017) are given in 25 °C. The reaction enthalpies for these reactions in 50 bar pressure and 25 °C are: $-40{,}9\frac{kJ}{mol}$, $-90{,}7\frac{kJ}{mol}$ and $42\frac{kJ}{mol}$ for Eqs. 2.3 – 2.5 respectively (Bertau et al., 2014).

The reactions are equilibrium reactions, meaning that the reactions can proceed to both directions depending on temperature, pressure and concentration of the reaction components. As seen from the reaction enthalpies, carbon monoxide hydrogenation and carbon dioxide hydrogenation reactions (Eqs. 2.3 and 2.4) are exothermic reactions in the forward direction, while the RWGS reaction (Eq. 2.5) is slightly endothermic. Also, the number of moles decrease in reactions 2.3 and 2.4 in the forward direction. According to Le Chatelier's principle, this suggests that the equilibrium concentrations in methanol synthesis favor the production of MeOH at low temperatures and high pressures (Bertau et al., 2014).

However, the reactions involved in the methanol synthesis are very slow to react on their own. For this reason, a catalyst is used. Typical catalytic materials used in traditional methanol synthesis from syngas are based on copper, zinc and aluminum oxides (Biedermann et al., 2006). Also, the reaction rate is very slow in low temperatures where the theoretical equilibrium conversion is high. Therefore, the operating temperature must be raised high enough for the methanol synthesis to reach closer to the equilibrium conversion. This means operating in temperatures where the equilibrium conversion is lower, but the reaction rate is faster. For this reason, in commercial processes it is wise to recycle the unreacted gases back to the reactor to improve the overall conversion (Bertau et al., 2014). The methanol synthesis process usually takes place in temperatures between 220 – 280 °C and in pressures between 40 – 110 bar in the presence of Cu/Zn/Al -based catalysts (Biedermann et al., 2006).

The output of the methanol synthesis is raw methanol. In addition to MeOH, raw methanol contains water, dissolved gases and some by-products. So, after methanol synthesis the raw

methanol needs to be purified. This happens in distillation columns, and the number of columns needed is determined by the quality requirements of the methanol product (Biedermann et al., 2006).

Methanol produced for chemical industry has higher requirements than methanol produced to be used as a fuel. There are different grades of methanol based on purity. Fuel grade methanol has the lowest requirements, where the only restriction is the minimum methanol content being 99 wt.%. A-grade methanol and AA-grade methanol have a higher minimum requirement of 99.85 wt.% MeOH for both, with AA-grade methanol having also stricter requirements for other impurities than A-grade methanol (Andika et al., 2018). The impurities are removed from crude methanol in the distillation process. Therefore, the production of A- and AA-grade methanol require more distillation columns than the production of fuel grade methanol. Purity grades with even stricter requirements exist, such as "CHROMASOLV methanol" which can be used for spectroscopic or semiconductor applications, having purity over 99.9 wt.% (Ott et al., 2000). However, AA-grade methanol is typical for chemical use.

2.2.1 Reactors for conventional methanol production

There are different types of reactor designs that can be used in conventional methanol synthesis. All the most commonly used commercial reactor types are fixed-bed reactors, that differ from each other mainly by their means of cooling. They are either adiabatic or approximately isothermal. The different reactor designs include quench reactors, adiabatic reactors, boiling water reactors and gas-cooled reactors. (Bertau et al., 2014).

Quench reactors consist of multiple adiabatic catalyst beds where the feed is divided between those beds in the reactor. The temperature of the reactor is controlled by controlling the reactor feed. The quench reactor design is very simple, but the catalyst beds being adiabatic makes it so that the reaction enthalpy released in the exothermic reaction raises the temperature of the stream when it approaches equilibrium. This lowers the equilibrium conversion resulting in lower per pass conversion (Biedermann et al., 2006). A simple quench reactor is described in Figure 7.

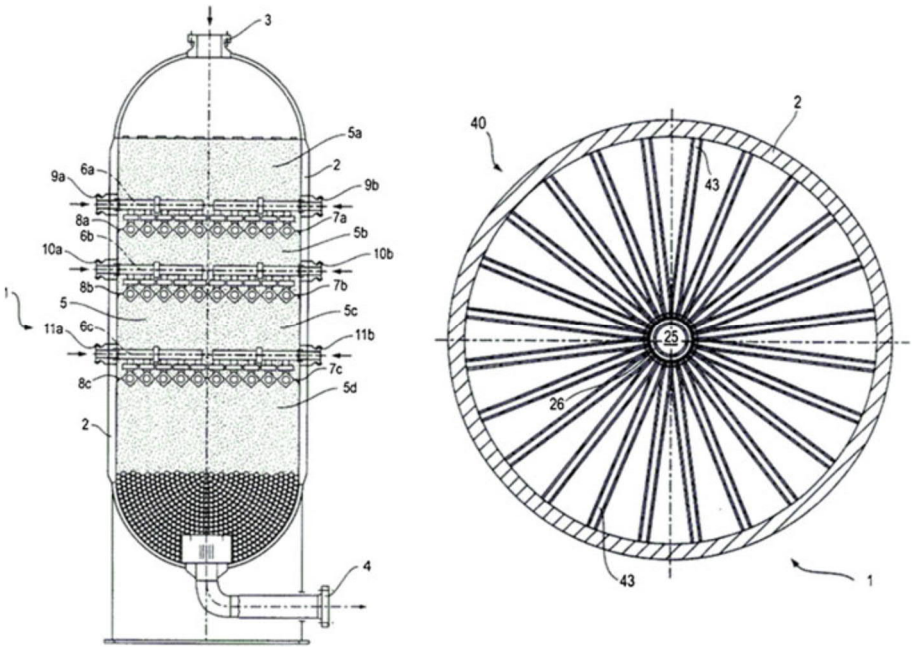


Figure 7. The simple quench reactor (Bertau et al., 2014)

Adiabatic reactor systems typically consist of multiple adiabatic reactors placed in series, with cooling achieved by heat being removed between reactors downstream after each reactor. Adiabatic reactor systems are easy to scale up, but they have the same disadvantage as the quench reactors of the high temperature resulting to lower per pass conversion (Biedermann et al., 2006). The Haldor Topsøe process with three adiabatic reactors is described in Figure 8. The methanol synthesis part of the process includes three adiabatic reactors in series with heat exchangers between the reactors for recovery of the endothermic heat of reaction (Bertau et al., 2014).

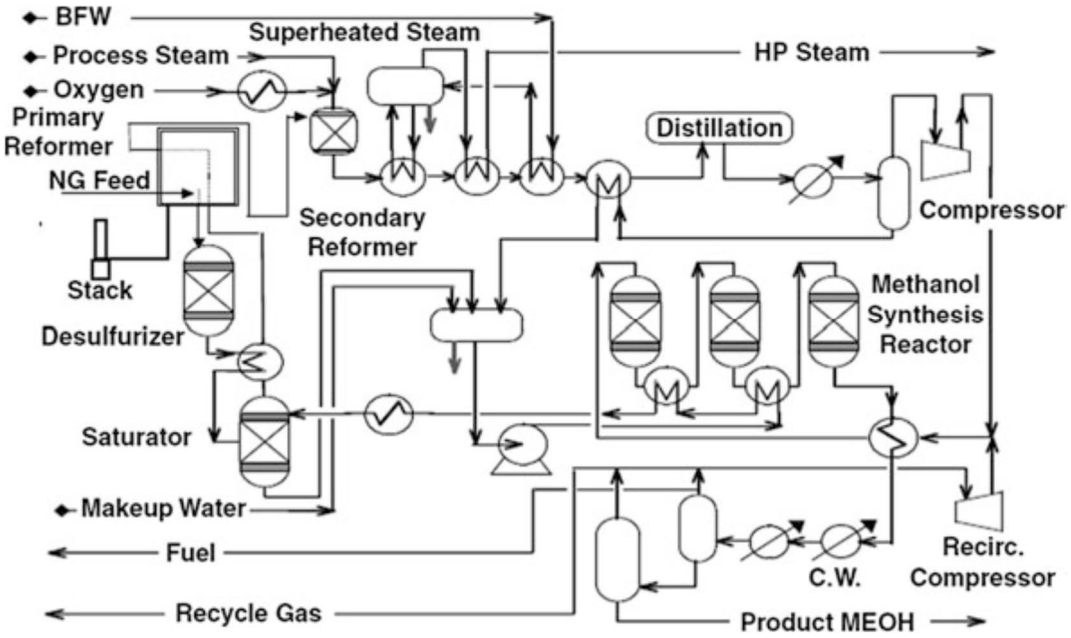


Figure 8. The Harold Topsøe adiabatic process design (Bertau et al., 2014)

Boiling water reactors have a design similar to that of shell and tube heat exchangers. They cool the reactor by circulating water at its boiling point around in the other side of the heat exchanging surface while cooling the reactants in the catalytic bed on the other side. Boiling water reactors are approximately isothermal reactors. The temperature can be controlled by controlling the pressure of the boiling water. Boiling water reactors usually operate in intermediate temperatures (240 – 260 °C), so, although less than in adiabatic reactor designs, significant recycling might still be needed. (Biedermann et al., 2006)

Gas-cooled reactors have the similar heat exchanger-like design than boiling water reactors. They are usually designed as being interconnected with boiling water reactors, so that the feed and effluent of the boiling water reactor are connected to the gas-cooled reactor. The gas-cooled reactor is cooled by the feed gas going in the boiling water reactor, while the feed is preheated simultaneously. The boiling water reactor effluent is brought to the catalyst side of the gas-cooled reactor, where it is cooled and can continue the methanol conversion to a higher equilibrium provided by the lower temperature. This helps achieve higher per pass conversions (Biedermann et al., 2006). The Lurgi combined reactor system described in Figure 9 represents the interconnected gas-cooled reactor and a boiling water reactor design (Bertau et al., 2014).

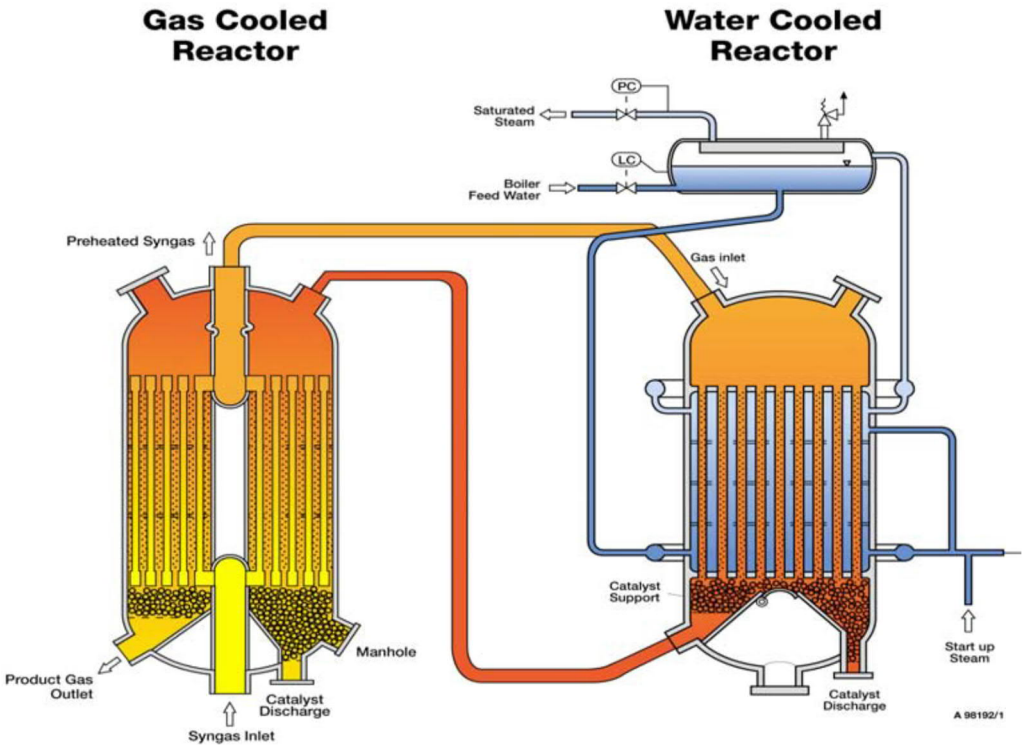


Figure 9. Lurgi combined reactor system includes a boiling water reactor and a gas-cooled reactor interconnected with each other (Bertau et al., 2014).

2.3 Methanol production from CO_2 and H_2

Instead of conventional methanol production that uses natural gas and other fossil sources as its feedstock, methanol production based on CO_2 and H_2 can provide a path to clean and sustainable methanol production. In this type of methanol production, syngas is replaced with a mixture of CO_2 and H_2. The CO_2 can be obtained from industrial flue gases, or even from air, via carbon capture technologies. The H_2 in turn can be generated from water via electrolysis using the excess electricity produced by renewable energy sources. This way the whole cycle from methanol production to its end use as a fuel would have a net zero carbon footprint. The process could be made carbon neutral, if all energy used in different steps of the process came from carbon free sources. This concept of methanol production from renewable sources is described in Figure 10 (Atsonios et al., 2016).

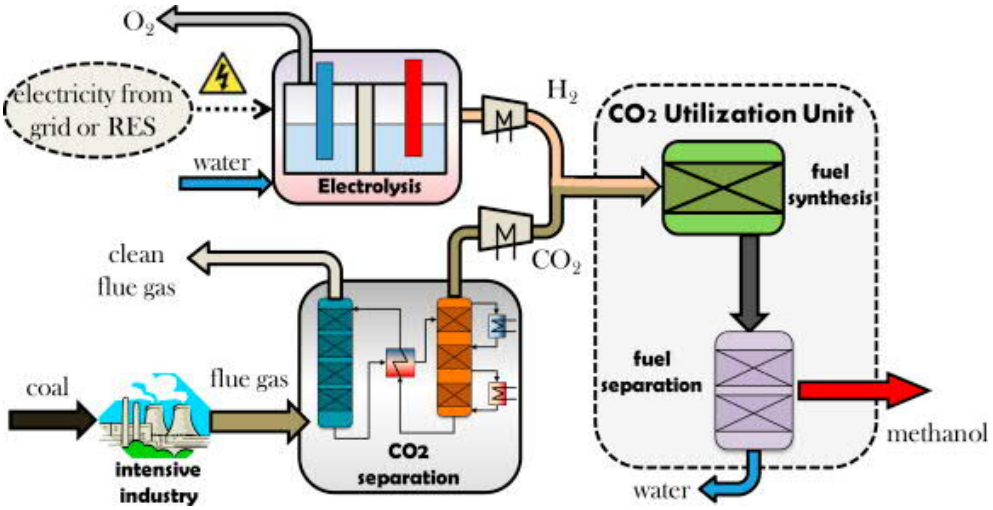


Figure 10. The renewable methanol production concepts (Atsonios et al., 2016).

The renewable methanol production process from CO_2 and H_2 described in Figure 10 includes four steps:

1. CO_2 separation from flue gas
2. H_2 production via water electrolysis
3. Methanol synthesis
4. Methanol distillation

The last two steps are very similar to those in conventional methanol production, but in this case the feed to the methanol synthesis is purely CO_2 and H_2. The exact same reactions described in Eqs. 2.3 – 2.5 that take place in syngas-based methanol synthesis also govern methanol synthesis from CO_2 and H_2. The steps 1 and 2 are described in chapters 2.3.1 and 2.3.2. The steps 3 and 4 are described in chapter 2.3.3.

2.3.1 Raw materials – CO_2

Carbon dioxide is one of the two main ingredients in carbon neutral methanol production concept together with hydrogen. CO_2 capture and storage (CCS) technologies have been gaining lots of attention due to their potential to have a significant impact in reducing the atmospheric CO_2 levels. CO_2 can be captured from emissions of industrial operations, or

directly from air. Because this is not the primary focus of our thesis, we will consider only CO_2 capture from industrial emissions in this chapter. For CO_2-based methanol production, efficient CO_2 capture technologies are essential for making the process sustainable. There are three basic routes for CO_2 capture from industrial operations (Thiruvenkatachari et al., 2009):

1. Pre-combustion capture
2. Oxy-fuel combustion
3. Post combustion capture

Pre-combustion capture involves reacting the fuel with oxygen to produce syngas. This syngas is then made to react with steam to create CO_2 from the CO and to further increase the H_2 content in the gas. Then the CO_2 is separated most commonly with some absorption process resulting in a hydrogen rich fuel that can be used in many applications. Oxy-fuel combustion means using only oxygen for combustion instead of air. This takes nitrogen out of the combustion process resulting in a flue gas mainly comprised of CO_2 and H_2O. In post combustion capture no changes are made to the fuel combustion process. After the combustion, the flue gas is conducted through CO_2 capturing equipment before releasing it to the atmosphere. From these three options, post combustion capture is the easiest to adopt because it does not require changes in the combustion process. (Thiruvenkatachari et al., 2009)

Different post combustion CO_2 capture technologies can be divided into different categories based on how they function. These include absorption, adsorption, cryogenic separation, membrane separation and micro algal bio-fixation technologies (Thiruvenkatachari et al., 2009). Different post combustion CO_2 capture technologies are presented in Figure 11.

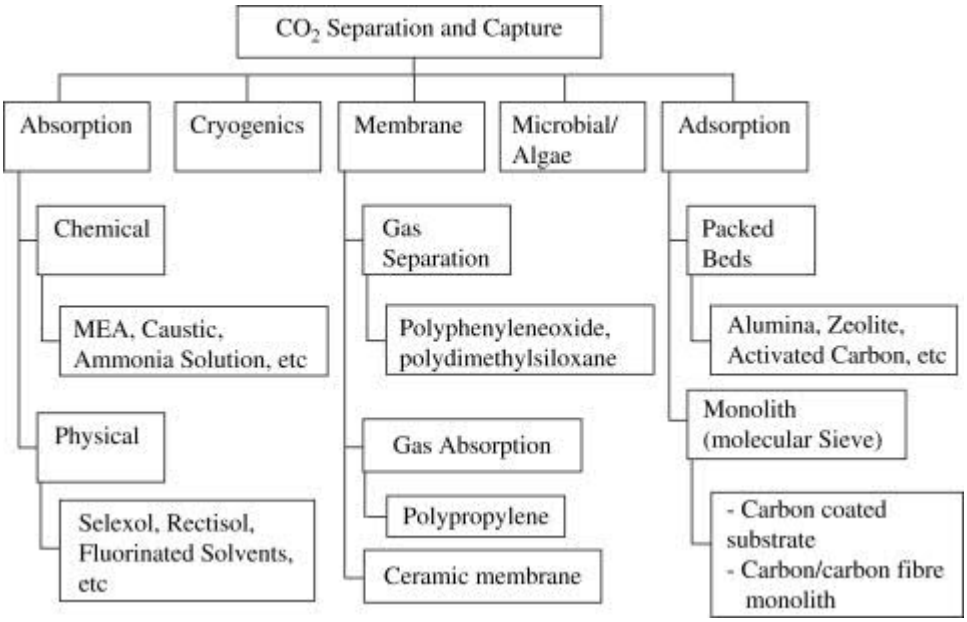


Figure 11. Different post combustion CO2 separation technologies (Thiruvenkatachari et al., 2009).

Currently the most mature CO_2 capture technology is the post combustion chemical absorption technology with amine rubbing, according to Atsonios et al. (2016). In this

technology the CO_2 collection from flue gas is done after combustion in a column via absorption. In the column, CO_2 is brought into contact with a monoethanolamine (MEA in Figure 11) aqueous solvent, and the following reaction occurs:

$$(CH_2)_2OHNH_2 + H_2O + CO_2 \leftrightarrow (CH_2)_2OHNH_3^+ + HCO_3^- \quad (2.6)$$

The products of the reaction described in Equation 2.6 are then carried in the solvent to the stripper unit, that operates in elevated temperatures. There CO_2 is then released from the solvent by the reverse reaction. The outlet of the stripper contains CO_2 and steam which are then separated by condensing the steam in ambient temperature (Atsonios et al., 2016).

2.3.2 Raw materials – H_2

Currently the most common method for hydrogen production is steam reforming of natural gas. However, a renewable methanol production concept requires the hydrogen to come from renewable sources. The electrolysis of water is the most mature technology to meet that criteria. In water electrolysis, H_2O is split into O_2 and H_2 using electricity according to the reaction presented in Equation 2.7. (Bertau et al., 2014)

$$2H_2O \rightarrow 2H_2 + O_2, \qquad \Delta_r H = 572 \frac{kJ}{mol} \quad (2.7)$$

There are three main electrolysis technologies: alkaline electrolysis, polymer electrolyte membrane electrolysis and high-temperature electrolysis. Among these the alkaline electrolysis is the most mature technology. (Atsonios et al., 2016)

Alkaline electrolysis is the oldest known water electrolysis technology. It is conducted in a solution of KOH (potassium hydroxide) with the following electrode reactions presented in Equations 2.8 and 2.9. Hydroxide ions pass through the diaphragm from cathode to anode in the process. The process is described in Figure 12. (Bertau et al., 2014)

$$Cathode\colon\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2.8)$$

$$Anode\colon\ 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (2.9)$$

The electrodes in alkaline electrolysis are usually nickel based. For this reason, alkaline electrolysis has low investment costs, since it requires no noble metals or expensive special alloys. However, the KOH electrolyte is very corrosive and affects the reaction kinetics negatively. Also, alkaline electrolysis plants have a long lag time in startup and shutdown, making them less suitable to use intermittent renewable electricity as an energy source. (Bertau et al., 2014)

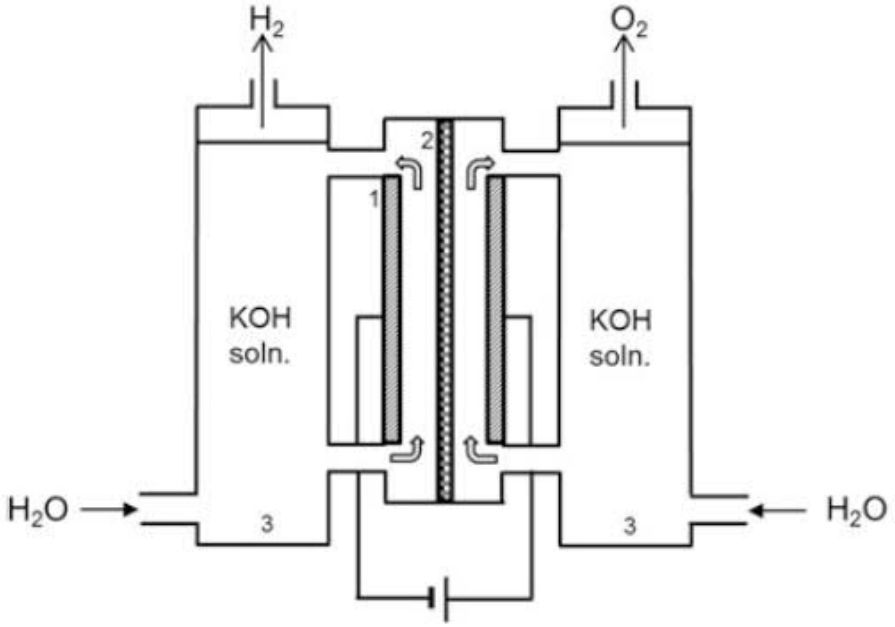


Figure 12. The alkaline water electrolysis process presented by Bertau et al. (2014). Numbers 1 indicate the electrodes (anode and cathode), number 2 the diaphragm and numbers 3 the gas-fluid separators.

Polymer electrolyte membranes (also referred as proton-exchange membranes or PEM) allow protons to pass through them from anode to cathode. The polymer electrolyte membrane electrolysis works by utilizing these proton-exchange membranes to split water into O_2 and H_2 with electricity and allowing the hydrogen ions (protons) to pass through the membrane. The reactions taking place in PEM electrolysis are presented in Equations 2.10 and 2.11. (Bertau et al., 2014)

$$Cathode\colon\ 4H^+ + 4e^- \rightarrow 2H_2 \tag{2.10}$$

$$Anode\colon\ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2.11}$$

Compared to alkaline electrolysis, PEM electrolysis has higher power efficiency and power density, allowing PEM electrolysis to achieve higher hydrogen production rates. PEM electrolysis is also more suitable to use intermittent renewable electricity as its power source than alkaline electrolysis (Bertau et al., 2014). However, it requires more expensive materials, such as platinum, making it more expensive and making its hydrogen production capacity harder to scale globally.

High-temperature electrolysis works in temperatures above 800 °C using solid oxide electrolysis cells (SOEC). In high-temperature electrolysis the oxygen ions travel from cathode to anode. In contrast to alkaline and PEM electrolysis, the H_2O used in high-temperature electrolysis is in gaseous form due to the high operating temperatures. The reactions taking place in high-temperature electrolysis are described in Equations 2.12 and 2.13. (Bertau et al., 2014)

$$Cathode:\ 2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-} \quad (2.12)$$

$$Anode:\ 2O^{2-} \rightarrow O_2 + 4e^- \quad (2.13)$$

Compared to alkaline and PEM electrolysis, SOEC has the potential to reach higher efficiencies. However, SOEC is still at a lab-scale phase in its development. (Andika et al., 2018)

2.3.3 Methanol synthesis from CO_2 and H_2

Methanol synthesis from CO_2 and H_2 is in many ways very similar to the conventional methanol synthesis from syngas. CO_2 -based methanol synthesis is governed by the same three equilibrium reactions as conventional methanol synthesis: CO_2 hydrogenation reaction, CO hydrogenation reaction and RWGS reaction (Eqs. 2.3 – 2.5).

To examine the characteristics of methanol synthesis from CO_2 and H_2, it makes sense to compare it with methanol synthesis from conventional syngas. One thing to consider, is the catalyst performance in CO_2 -based methanol synthesis. All these reactions (Eqs. 2.3 – 2.5) take place on the surface of the catalyst inside the reactor. Since the reactions are same as in conventional methanol synthesis, similar Cu/Zn/Al -based catalysts can be used for methanol synthesis from CO_2 and H_2. (Bertau et al., 2014)

Pontzen et al. (2011) conducted experiments where they performed methanol synthesis both from CO_2 -based syngas and standard syngas and compared the results. They used the same equipment and catalyst for both feed gas types. The catalyst used was described as "a commercial Cu/ZnO catalyst (Süd-Chemie, Germany)" by Pontzen et al. (2011). The experiments were conducted in a loop reactor, with built in recirculation for unreacted gases. In their setup, the product mixture consisting of H_2, CO_2, CO, H_2O and $MeOH$ was cooled after the reactor, and the liquid products were separated from the gases. The remaining gases were then mixed with make-up gas from the original feed gas inlet and recycled back to the reactor. This recycle system for unreacted gases is a common component in methanol synthesis reactors.

Pontzen et al. (2011) operated the reactor at very similar conditions for both feeds. With their CO_2 -based syngas the reactor was operated at 250 °C temperature and 80 bar pressure. With their standard syngas, the reactor was operated at 250 °C and 70 bar. The slightly lower pressure for standard syngas was used to avoid high peak temperatures for reasons explained later. In the experiment, the reactor was operated continuously, altering the feed gas between CO_2 -based syngas and standard syngas in the middle of the experiment. A common unit used to describe the gas flow rate in a reactor is gas hourly space velocity (GHSV). It describes the rate of feed gas flow over a unit portion of the catalyst over time, usually expressed in units: $\frac{L_{feed\ gas}}{L_{catalyst} \times h}$ or just h^{-1}. The GHSV used by Pontzen et al. (2011) was 10 500 h^{-1} for both CO_2 -based syngas and standard syngas. The experimental conditions used by Pontzen et al. (2011) are presented in Table 1.

Table 1. Process conditions used by Pontzen et al. (2011)

Feed	*Temperature (inlet) (°C)*	*Temperature (peak) (°C)*	*Pressure (bar)*	*GHSV (h^-1)*	*Test duration (h)*
Standard syngas	250 °C	283	70	10 500	100
CO_2 -based syngas	250 °C	264 – 260	80	10 500	700

There are three main requirements from a catalyst: activity, selectivity and stability. To evaluate the performance of a catalytic process, these three things need to be considered. Catalyst activity means simply the ability of the catalyst to catalyze the reactants into products via the reaction pathways. Higher activity therefore leads to higher yield. Selectivity of the catalyst means the tendency of the catalyst to catalyze a certain product over others. Higher selectivity leads to less by-product formation. The stability of the catalyst describes its durability. Higher stability results in lower catalyst deactivation and therefore longer lifetime of the catalyst. The CO_2 -based methanol synthesis can be analyzed by reviewing the results obtained by Pontzen et al. (2011) with these three main requirements for catalyst in consideration.

To compare the catalyst activity in CO_2 -based syngas and standard syngas, we can analyze the space time yield achieved with these two feed gases. Space time yield (STY) represents the amount of methanol produced per amount of catalyst per hour and is usually expressed as $\frac{kg_{MeOH}}{L_{catalyst} \times h}$. The STY results obtained by Pontzen et al. (2011) were around 0.6 $\frac{kg_{MeOH}}{L_{catalyst} \times h}$ for CO_2 -based syngas and around 0.9 $\frac{kg_{MeOH}}{L_{catalyst} \times h}$ for standard syngas suggesting higher activity for standard syngas. The STY results by Pontzen et al. (2011) are presented in Figure 13. These findings seem to suggest methanol synthesis from standard syngas to be faster than methanol synthesis from CO_2 and H_2.

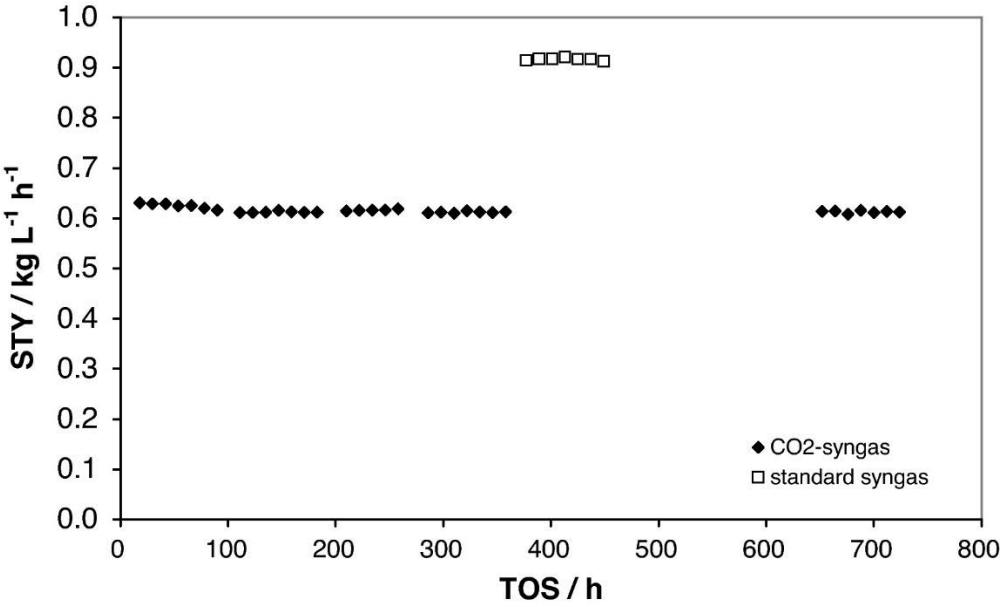


Figure 13. STY achieved with CO2 -based syngas and standard syngas by Pontzen et al. (2011). (TOS = Time on stream)

The selectivity to methanol can be examined as an overall selectivity, or as selectivity to methanol excluding water. The overall selectivity to methanol means just the amount of methanol produced compared to everything else produced by the system. When using a feed gas containing CO_2 and H_2, both primary reactions (CO_2 hydrogenation and RWGS) will form water into the reactor. This means that water will take up a large fraction of the total products. The crude methanol produced from CO_2 and H_2 contains 30 – 40 % of water by gravimetric basis (Bertau et al., 2014).

However, excluding water methanol synthesis from CO_2 and H_2 produces much fewer other by-products than conventional methanol synthesis. This has at least some to do with the by-product forming reactions having high temperature sensitivity. As seen from the reaction enthalpies, CO_2 hydrogenation reaction is less exothermic than CO hydrogenation reaction. Also, RWGS reaction is endothermic. The exothermic effect of the CO_2 hydrogenation reaction is only slightly higher than the endothermic effect of the RWGS reaction, resulting only in a marginal temperature increase in the catalyst bed. This lower total exothermic effect results in a lower peak temperature in the catalyst in CO_2 -based methanol synthesis than in methanol synthesis from syngas. Most of the by-products are mainly formed at higher temperatures (Bertau et al., 2014). This results in lower by-product formation in CO_2 -based methanol synthesis.

The results of Pontzen et al. (2011) support these statements. The water content was remarkably higher in CO_2 -based methanol synthesis compared to standard syngas-based methanol synthesis, while the content of other impurities was much lower. The results from Pontzen et al. (2011) are presented in Table 2. However, Pontzen et al. (2011) also found that the by-product concentration (excluding water) was much lower for CO_2 -based syngas even with comparable peak temperature levels. It seems that methanol synthesis from CO_2 and H_2 is more selective overall compared to conventional methanol synthesis (excluding water formation). This is important, because as in conventional methanol production, the

crude methanol requires distillation also in CO_2 -based methanol production. Water is easier to separate from crude methanol, whereas the separation of other by-products (especially ketones) is much harder (Pontzen et al., 2011). Lower by-product concentration therefore makes the distillation process easier in CO_2 -based methanol production.

*Table 2. Purity of the crude methanol from the pilot plant experiments by Pontzen et al. (2011). The values in brackets marked with the *-symbol represent the selectivity excluding water.*

Feed	*Process conditions*	*Overall selectivity to MeOH (%)*	*Water content (%, wt.)*	*Other by-product content (ppm, wt.)*
Standard syngas	250 °C, 70 bar	87.0 (99.82)*	12.8	1800
CO_2 -based syngas	250 °C, 80 bar	63.9 (99.96)*	36.1	390

The most common liquid by-product is of course water. Other by-products found in the liquid crude MeOH may include some higher alcohols such as ethanol, propanol and butanol. Other by-products such as methyl formate may also be present. The alcohols are generated by different CO hydrogenation reactions (Bertau et al., 2014). Experiments conducted by Ushikoshi et al. (1998) on their pilot plant for methanol production from CO_2 and H_2 produced methyl formate, ethanol, 1-propanol, 2-propanol and 2-butanol (and water) as by-products in the liquid crude methanol. Other by-products are produced as gas and do not end up in the liquid crude methanol. Most notably CO can be viewed as a by-product produced with RWGS reaction. Other by-products found in gas by Ushikoshi et al. (1998) were: water, DME, methane, methyl formate, ethane and ethanol. However, Bertau et al. (2014) note that methane should not be formed as a by-product as it needs a completely different catalyst. DME is a derivative of methanol and is often a preferred product. DME is formed from MeOH with the reaction presented in Equation 2.14 (Pontzen et al., 2011).

$$2CH_3OH \leftrightarrows CH_3OCH_3\ (DME) + H_2O \tag{2.14}$$

The last thing to consider is the stability of the catalyst. Deactivation can occur in the catalyst meaning the catalyst will lose its ability to catalyze the reactions. When methanol is produced from syngas the primary deactivation mechanism is poisoning by sulfur and chloride traces being present in the feed gas. Therefore, it is important to remove the sulfur containing components from natural gas before the synthesis gas production process. In methanol synthesis from CO_2 and H_2 the main cause for catalyst deactivation is the large amount of water generated by the RWGS reaction. The presence of steam accelerates the growth of copper crystals which deactivates the catalyst. (Bertau et al., 2014)

On the other hand, also thermal stress causes catalyst deactivation by formation of larger copper crystallites. As pointed out, methanol synthesis from CO_2 and H_2 is less exothermic and therefore releases less energy heating up the catalyst less than conventional methanol

production. This lower exothermic effect in CO_2 -based methanol synthesis reduces the thermal stress experienced by the catalyst, therefore reducing the deactivation of the catalyst. (Bertau et al., 2014)

Pontzen et al. (2011) concluded that under similar conditions, the CO_2 -based methanol synthesis is slower but more selective than syngas-based methanol synthesis. This allows higher temperatures to be used in CO_2 -based methanol synthesis without it having too much of an impact on selectivity. This makes the distillation process easier, as the larger amounts of water generated in CO_2 -based methanol synthesis are much easier to separate from MeOH than other by-products. Also, less cooling of the synthesis process is needed when using a CO_2 -based feed gas.

The clear downside of methanol production from CO_2 and H_2 is the lower conversion to methanol. This can be solved by implementing a re-circulation for unreacted gases back to the reactor. On an industrial scale, the selectivity and stability of the catalyst system are important. Lower conversion rates can be accepted if the recycling of unreacted gases back to the process is efficient. This makes CO_2 -based methanol production an attractive alternative to conventional methanol production on its own, since its by-product formation is lower. The catalyst deactivation due to the presence of H_2O in the reactor is an issue still in the need to be solved. However, with lower per pass conversions that are compensated with re-circulation, there is also less per pass water formation, which should reduce the catalyst deactivation rate. (Bertau et al., 2014)

The main working principle of the catalyst is adsorption. According to Graaf et al. (1988) there are two surfaces in the traditional Cu/Zn/Al -catalyst that adsorb different molecules and atoms. Let's call those sites s_1 and s_2. On s_1 CO and CO_2 adsorb competitively, whereas on s_2 H_2 and H_2O adsorb competitively. H_2 is adsorbed dissociatively, which means that the two hydrogen atoms in H_2 are adsorbed on two s_2 surfaces separately. However, Lim et al. (2009) suggested different adsorption sites for CO and CO_2, as according to them, the copper is reduced or oxidized in the adsorption of CO and CO_2 respectively. They refer the site where CO adsorbs as s_1 and the site where CO_2 adsorbs as s_3. They state that the adsorption site s_1 represents Cu^{1+} and site s_3 represents Cu^0. According to them s_2 where hydrogen adsorbs is the site of ZnO. Lim et al. (2009) presents the elemental reactions happening on a $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst surface for CO_2 hydrogenation reaction, CO hydrogenation reaction and RWGS. These elemental reactions are presented in Tables 3 – 5 respectively. It is good to note that these same elemental reactions take place not only in methanol synthesis from CO_2 and H_2 but also in methanol synthesis from syngas.

Table 3. Elemental reactions for CO_2 hydrogenation reaction [presented in eq. 2.3] (Lim et al., 2009)

Step 1:	$CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows HCO_2 \cdot s_3 + s_2$
Step 2:	$HCO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows H_2CO_2 \cdot s_3 + s_2$
Step 3:	$H_2CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows H_3CO_2 \cdot s_3 + s_2$
Step 4:	$H_3CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows H_2CO \cdot s_3 + H_2O \cdot s_2$
Step 5:	$H_2CO \cdot s_3 + H \cdot s_2 \rightleftarrows H_3CO \cdot s_3 + s_2$
Step 6:	$H_3CO \cdot s_3 + H \cdot s_2 \rightleftarrows CH_3OH + s_3 + s_2$

Table 4. Elemental reactions for CO hydrogenation reaction [presented in eq. 2.4] (Lim et al., 2009)

Step 1:	$CO \cdot s_1 + H \cdot s_2 \rightleftarrows HCO \cdot s_1 + s_2$
Step 2:	$HCO \cdot s_1 + H \cdot s_2 \rightleftarrows H_2CO \cdot s_1 + s_2$
Step 3:	$H_2CO \cdot s_1 + H \cdot s_2 \rightleftarrows H_3CO \cdot s_1 + s_2$
Step 4:	$H_3CO \cdot s_1 + H \cdot s_2 \rightleftarrows CH_3OH + s_1 + s_2$

Table 5. Elemental reactions for reverse water−gas shift reaction [presented in eq. 2.5] (Lim et al., 2009)

Step 1:	$CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows HCO_2 \cdot s_3 + \cdot s_2$
Step 2:	$HCO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows CO \cdot s_3 + H_2O \cdot s_2$

There is not a scientific consensus whether carbon dioxide reacts with hydrogen directly or phase by phase, first converting to CO via RWGS reaction and then to methanol by CO hydrogenation reaction). That is why both reaction pathways are described in Tables 3 – 5. This has been studied by many (Graaf et al., 1988; Lim et al., 2009), to name a few, but the exact reaction mechanism is still debated. This topic is discussed and analyzed in more detail in chapter 3 of this thesis.

2.3.4 CO_2 -based methanol production plants

Lurgi was the first to demonstrate converting CO_2 to methanol with their pilot plant in 1994. The key to their success was a new Cu/Zn/Al -catalyst developed by Süd-Chemie, now known as Clariant. The catalyst had high activity for converting CO_2 to methanol, which permitted high loads and therefore high space-time yields (STY explained thoroughly in chapter 3). (Bertau et al., 2014)

In their reactor concept Lurgi aimed to offset the drawbacks of lower equilibrium conversion of CO_2 -based methanol synthesis by dividing the reaction system into two separate reactor units: RWGS unit and methanol synthesis unit. This was done by feeding the mixture of CO_2 and H_2 to an adiabatic single-pass reactor. In the adiabatic reactor, some of the CO_2 and H_2 is converted to CO and H_2O via RWGS reaction and some to MeOH and H_2O via CO_2 hydrogenation reaction. The process is described in Figure 14. The adiabatic reactor does not require cooling because as previously discussed, the exothermic effect of the CO_2 hydrogenation reaction is only slightly higher than the endothermic effect of the RWGS reaction, resulting only in a marginal temperature increase in the catalyst.

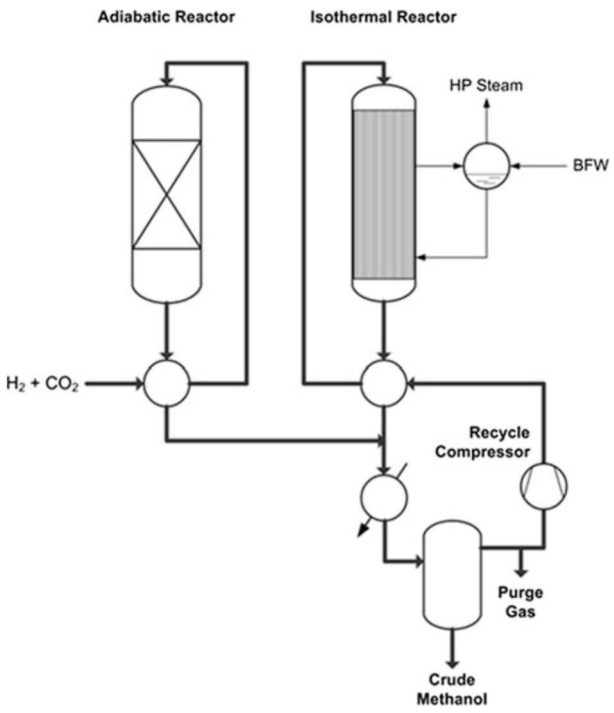


Figure 14. The Lurgi CO_2 and H_2 -based methanol production process (Bertau et al., 2014)

The output gas of the adiabatic reactor is then cooled and fed to the isothermal reactor loop. There the liquids (MeOH and H_2O) are first separated from the stream after which the gases are fed to the water-cooled isothermal reactor where the reaction temperature can be controlled. The adiabatic reactor is operated at 80 bar pressure and 240 – 280 °C temperature whereas the isothermal reactor is operated at 78 bar pressure and 270 °C. The same Cu/Zn/Al-catalyst is used both in the adiabatic and the isothermal reactor. (Bertau et al., 2014)

Another process type for converting CO_2 to methanol is the CAMERE process developed in Korea. Like the Lurgi process design, CAMERE also consists of two separate reactors. First the CO_2 is converted to CO and H_2O in the RWGS reactor. Then water is removed from the product gas mixture and the resulting gas mixture containing CO_2, H_2 and CO is then fed into the methanol reactor. Both the RWGS reactor and the methanol reactor have their own

recycling loops to increase the conversion of CO_2 to CO and methanol (Bertau et al., 2014). The CAMERE process is described in Figure 15.

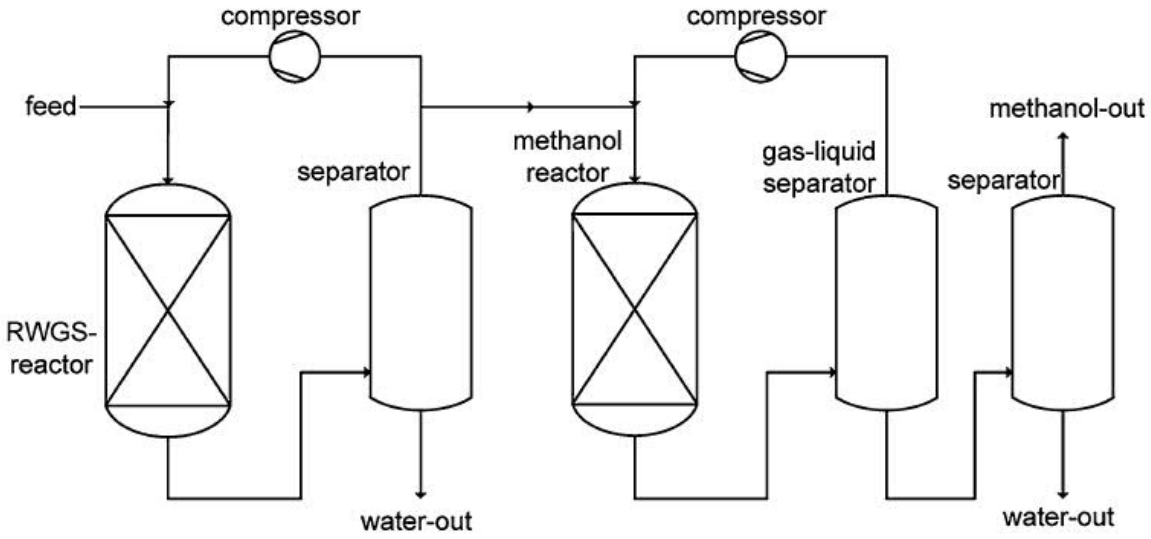


Figure 15. The CAMERE methanol production process. (Bertau et al., 2014)

The key advantage of the CAMERE process is the removal of water between reactors. As discussed, water can lead to catalyst deactivation, and the removal of water also shifts the reaction equilibrium towards products. The pilot plant has the methanol production capacity of 100 kg per day. (Bertau et al., 2014)

Mitsui Chemicals Inc. built a plant to Osaka, Japan for methanol synthesis from CO_2 that has been operating since 2009 (Bertau et al., 2014). The Mitsui plant has a methanol production capacity of 100 tons per year. Their methanol production concept is to get their supply consists of CO_2 emitted by factories and H_2 produced by water photolysis (Andika et al., 2018). So, even though they do not use electricity for H_2O splitting, their H_2 production is based on renewable energy sources. The concept level picture of the Mitsui methanol plant is presented in Figure 16.

The Mitsui process uses a catalyst composed of oxidized copper, zinc, aluminum, zirconium and silicon. The catalyst was developed for CO_2 and H_2 -based methanol synthesis together with the Research Institute of Innovative Technology for the Earth (RITE) in Japan. RITE also developed a pilot plant with a 50 kg/day methanol production capacity together with the National Institute for Resources and Environment (NIRE), that was used in the 1990's for multicomponent catalyst studies for methanol synthesis from CO_2 and H_2 in Japan. One study by Ushikoshi et al. (1998) that utilizes this pilot plant is examined in the literature review in chapter 4.3 of this thesis. However, this pilot plant built by RITE and NIRE is not the same as the Mitsui plant. Overall there is little information available of the Mitsui methanol synthesis process design. (Andika et al., 2018; Bertau et al., 2014)

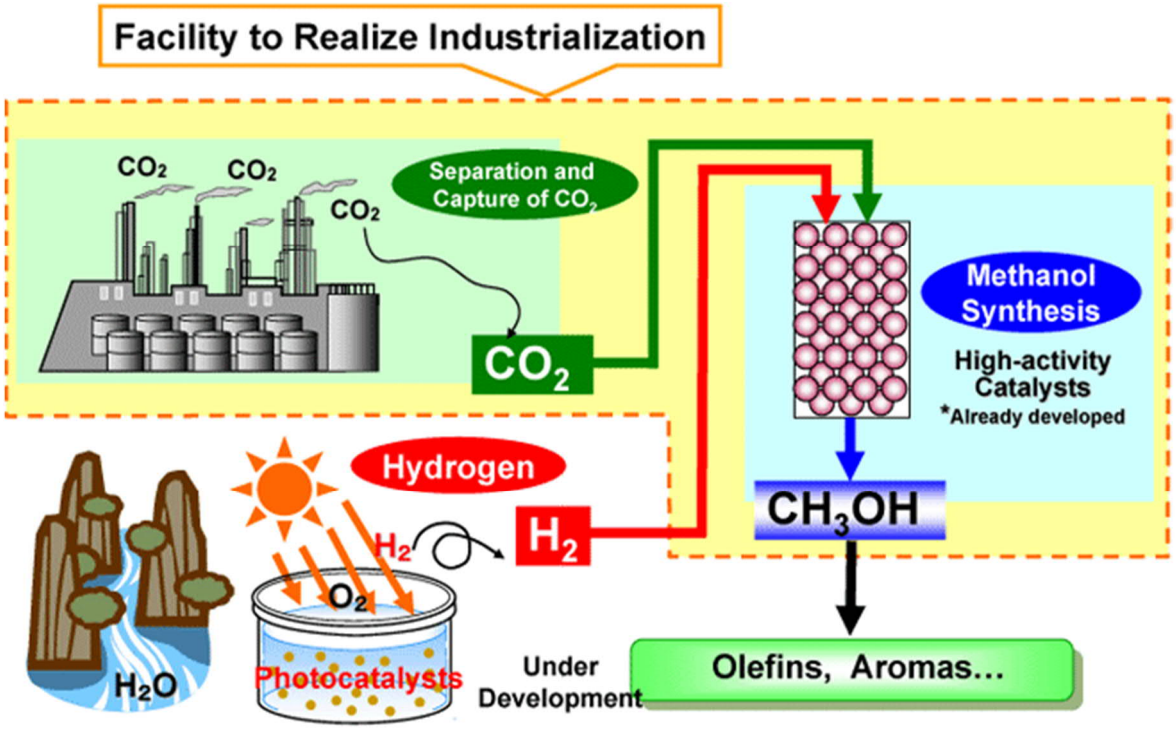


Figure 16. Mitsui carbon neutral methanol production concept. (Mitsui Chemicals, n.d.)

Carbon Recycling International (CRI) constructed a plant in Iceland that uses CO_2 and H_2 for methanol production. The "George A. Olah Renewable Methanol Plant" (named after George Olah, the Nobel laureate in chemistry) was completed in 2011. CRI uses geogenic CO_2 and geothermal heat to produce methanol (Bertau et al., 2014). The H_2 is produced via water electrolysis with renewable electricity (Andika et al., 2018). The plant was originally intended to produce 2 million liters of methanol annually (Bertau et al., 2014), but CRI increased the plant capacity to 5 million liters in 2015. The methanol they produce have a registered brand name – Vulcanol™ (Andika et al., 2018). From the three CO_2 -based methanol plants presented in this chapter, the CRI plant is the only commercial plant in operation, whereas the Lurgi plant and the CAMERE plant were rather on a demonstration scale.

3 Reaction analysis and equilibrium model for CO_2 hydrogenation

3.1 Analysis of the carbon source of methanol

As mentioned in chapter 2.3.3, the exact reaction mechanism for methanol synthesis is still unclear. One of the main disagreements in literature, is whether the primary source of methanol is CO_2 or CO meaning whether CO_2 converts to methanol directly via CO_2 hydrogenation or whether it first converts to CO via RWGS and then to MeOH via CO hydrogenation. In this chapter, we are going to look at what arguments have been presented when different authors have attempted to provide their answer to this question.

Bozzano & Manenti (2016) provided a list of studies ranging from 1970 to 2014 (Table 2 in their paper) where the carbon sources of methanol were discussed and whether the carbon source proposed by the authors was CO, CO_2 or both in these studies. We grouped these studies listed by Bozzano & Manenti (2016) by the decade they were made and found an interesting pattern. As seen from Figure 17, CO was considered the only source of methanol in the 70's and 80's, but this point of view has not been present in studies since the 90's. More recent studies consider usually either CO_2 as the primary source of MeOH, or consider both CO_2 and CO as significant sources. Based on this it is implied that it is very likely for CO_2 hydrogenation to occur on its own without the need for the intermediate step of converting to CO via RWGS.

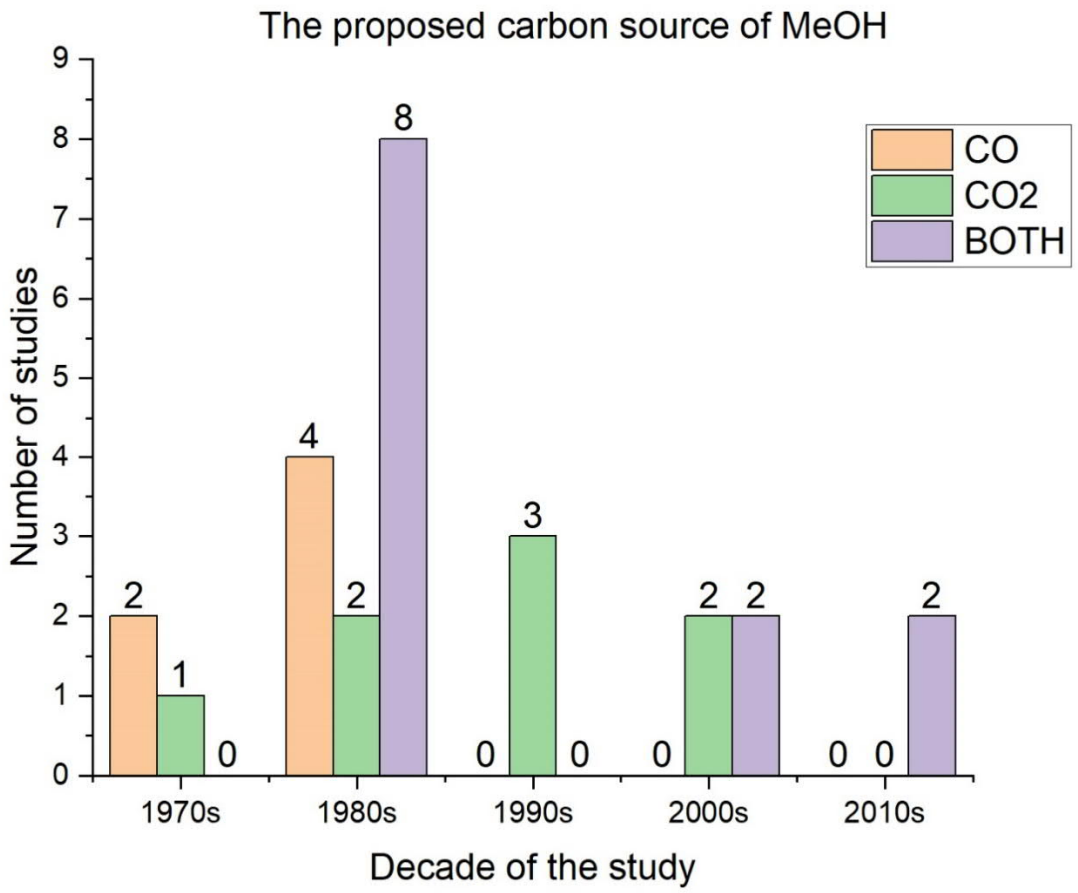


Figure 17. The carbon source of methanol proposed by different authors listed by Bozzano & Manenti (2016) categorized by the decade of the publication.

Some isotope experiments have been performed to find out the primary source of methanol. Chinchen et al. (1987) conducted one of these isotope experiments and found that with all practical gas mixtures containing CO_2, CO and H_2 the methanol was predominantly produced from CO_2 when using a $Cu/ZnO/Al_2O_3$ catalyst, with CO hydrogenation occurring only with very low levels of CO_2 and with oxygen being absorbed on the copper in the catalyst. They also concluded that CO_2 hydrogenation and RWGS reactions shared no common surface intermediate that contained carbon. This is contradictory to how the intermediate reactions are presented in Tables 4 – 6 (Lim et al., 2009), where formate (HCO_2) is presented as the first surface intermediate for both CO_2 hydrogenation and RWGS reaction.

Grabow & Mavrikakis (2011) conducted an extensive study where they examined the activation energies of different surface reactions in a catalyst to analyze the reaction pathways taking place in methanol synthesis. They built a microkinetic model of methanol synthesis using density functional theory, including the reaction energetics of 49 elementary steps. Grabow & Mavrikakis (2011) found that under typical industrial conditions, 2/3 of methanol is produced by CO_2 hydrogenation. They described the typical reaction conditions as 230 – 280 °C and 50 – 120 atm.

Studt et al. (2015) also studied the topic from the point of view of the activation energies of the different reactions. They suggested that the presence of formate (HCOO*, the surface intermediate HCO_2 discussed previously) plays a key role in methanol synthesis kinetics. According to Studt et al. (2015), the selection of the catalyst makes a big difference on the reaction pathway which the methanol synthesis overgoes. They found that Cu catalysts can catalyze CO conversion at fast rate in the absence of ZnO, but they deactivate because of the increasing formate concentration. Studt et al. (2015) regarded formate as the main species on the catalyst surface, and this was also stated by Biedermann et al. (2006). Studt et al. (2015) then go on to propose that the presence of ZnO, blocks the CO conversion sites, resulting in poor CO conversion rate, while simultaneously increasing the binding of CO_2, making Cu/ZnO catalysts good for feeds consisting mainly of CO_2. The findings of Studt et al. (2015) are presented in Figure 18.

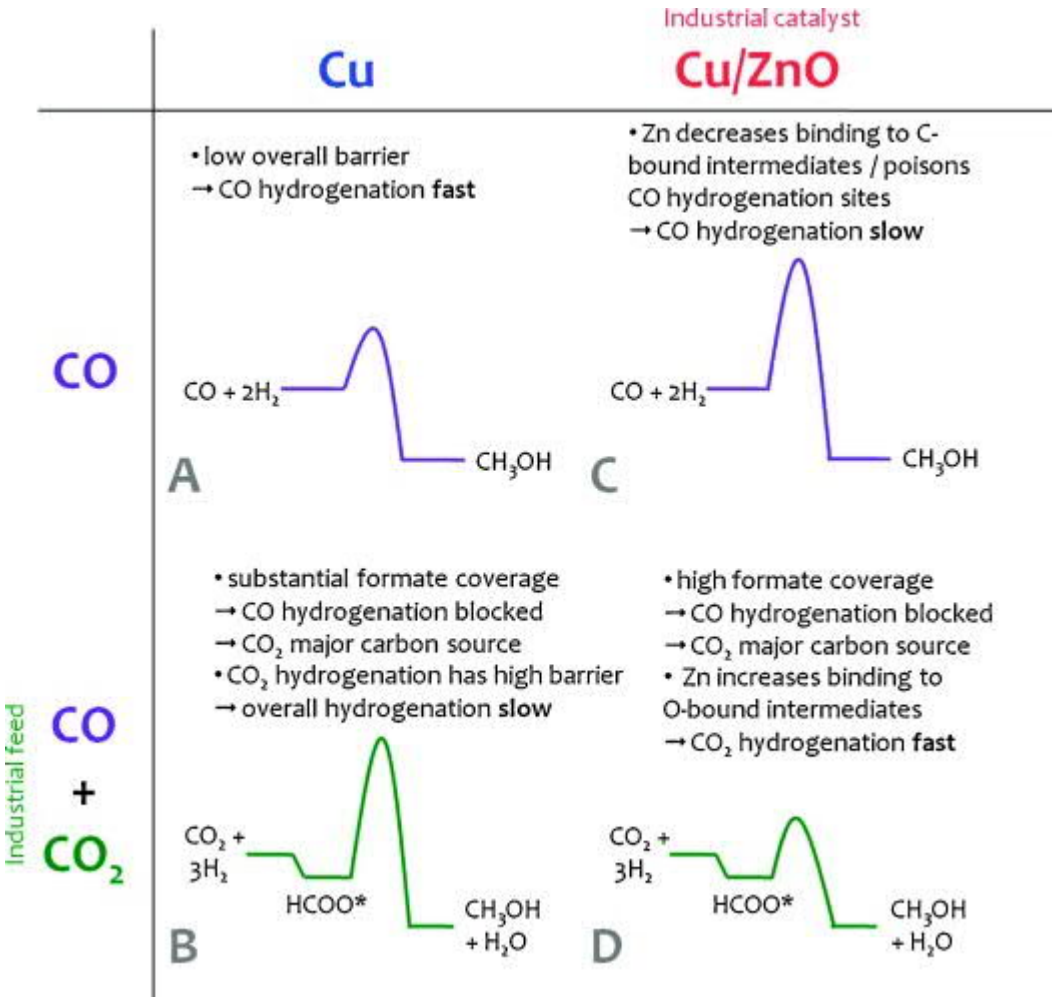


Figure 18. Activation energies for different feed gas compositions and different catalysts studied by Studt et al. (2015).

These findings by Studt et al. (2015) suggest, that the reaction kinetics and pathways depend on the catalyst and feed gas composition. Therefore, it might not be fruitful to try to explain the reaction kinetics only with the experimental results of the reaction rates. For example the statement: "Experimental studies show, when both CO and CO_2 are present, that CO_2 is the main source of methanol under usual conditions over $Cu/ZnO/Al_2O_3$ catalysts" (Portha et al., 2017) while correct, might not provide a full picture of the complex phenomenon.

3.2 The equilibrium model for CO_2 hydrogenation

In this thesis we created a model to estimate the methanol yield at thermodynamic equilibrium. It seems that CO_2 hydrogenation can be reasonably assumed as the primary route for methanol generation, especially when using a feed gas composed exclusively of CO_2 and H_2. For this reason, to create a simple model to present the methanol yield at thermodynamic equilibrium, we took only CO_2 hydrogenation reaction into account.

For CO_2 hydrogenation reaction the equilibrium constant is defined in Equation 3.1 as:

$$K = \frac{a_{MeOH} \times a_{H_2O}}{a_{CO_2} \times a_{H_2}^3} \tag{3.1}$$

where a_{MeOH}, a_{H_2O}, a_{CO_2} and a_{H_2} are activities for methanol, water, carbon dioxide and hydrogen respectively. To simplify the calculations, we are assuming ideal gas behavior for all gases in the reactor conditions. With the ideal gas assumption, we can express the equilibrium constant with partial pressures and eventually, with molar fractions and total pressure as shown in Equation 3.2:

$$a_i = \frac{p_i}{p_0} = \frac{x_i p}{p_0} \tag{3.2}$$

Here x_i represents the molar fraction of the component at the equilibrium, p is the total pressure of the system and p_0 is the pressure at standard conditions (1 bar). The equilibrium constant becomes:

$$K = \frac{x_{MeOH} \times x_{H_2O}}{x_{CO_2} \times x_{H_2}^3} \times \left(\frac{p}{p_0}\right)^{-2} \tag{3.3}$$

We can simplify Equation 3.3 by utilizing the things we know. Our feed consists of 25 mol-% CO_2 and 75 mol-% H_2. Therefore, we know: $x_{H_2} = 3x_{CO_2}$ regardless of how much CO_2 has been converted into MeOH in equilibrium. Similarly, as water and MeOH are generated equally, we can represent: $x_{H_2O} = x_{MeOH}$ regardless of conversion. However, the relationship between CO_2 and MeOH is more complicated. In total molar amounts the following relationship presented in Equation 3.4 applies:

$$n_{MeOH,equilibrium} = n_{CO_2,beginning} - n_{CO_2,equilibrium} \tag{3.4}$$

where $n_{MeOH,equilibrium}$ and $n_{CO_2,equilibrium}$ represent the equilibrium molar amounts for MeOH and CO_2 respectively, while $n_{CO_2,beginning}$ represents the molar amount of CO_2 in the beginning when only CO_2 and H_2 are present.

However, this relationship does not exist between the molar fractions, as molar fractions represent the molar amount of a compound in relation to the total molar amount of all compounds in the system. In CO_2 hydrogenation reaction, the total number of gas moles is halved. In case of 20 % CO_2 conversion to methanol for example, the total amount of MeOH moles in the end would be exactly 20 % of the total number of CO_2 moles in the beginning.

However, the mole fraction of MeOH in the end would be more than 20 % of the mole fraction of CO_2 in the beginning, since there would be 10 % less gas moles in total in the end. Because of this, it is useful to represent the molar fractions of CO_2 and MeOH as a function of the conversion % of CO_2 to MeOH, represented as $conv.\%$. As this model takes only into account the CO_2 hydrogenation reaction, there is no distinction between CO_2 conversion and methanol yield, as they mean the same. The molar fractions as function of $conv.\%$ are presented in Eqs. 3.5 – 3.8.

$$x_{CO_2} = \frac{1 - conv.\%}{2 \times (2 - conv.\%)} \tag{3.5}$$

$$x_{H_2} = 3 \times x_{CO_2} \tag{3.6}$$

$$x_{MeOH} = \frac{conv.\%}{2 \times (2 - conv.\%)} \tag{3.7}$$

$$x_{H_2O} = x_{MeOH} \tag{3.8}$$

Plugging in these formulas to an Excel-sheet for x_{CO_2}, x_{H_2}, x_{MeOH} and x_{H_2O}, we can use Equation 3.3 to find the equilibrium methanol yield. First, we decide at which pressure we want to analyze the equilibrium: we select $p = 50\ bar$. Then, we move everything on one side of the equation, creating an equation where the right-hand side is 0. Now all we need is to find values for the equilibrium constant K. For that we use two literature sources: (Graaf et al. 1986) and (Haynes et al. 2014, as presented in: Graaf & Winkelman 2016). These sources give us K values for CO hydrogenation reaction and RWGS reaction. According to these sources, the equilibrium constant K for CO_2 hydrogenation reaction can be obtained by multiplying these K values for the two reactions with each other, as the CO_2 hydrogenation reaction can be expressed as a combination of those two reactions.

First thing to note is that the value of the equilibrium constant depends on the reaction temperature. Graaf & Winkelman (2016) list literature values for the equilibrium constant K for the CO hydrogenation reaction and RWGS reaction in different temperatures from different sources. For this analysis we used the values from Haynes et al. (2014) presented by Graaf & Winkelman, because they had listed also “plus” and “minus” values for K that they got by over- or underestimating the change of Gibbs energy at the standard state. Graaf et al. (1986) on the other hand offers two equations (presented in Equations 3.9 and 3.10) that can be used to roughly estimate K for CO hydrogenation reaction (with Eq. 3.9) and RWGS reaction (with Eq. 3.10) as a function of temperature.

$$\log_{10} K_{p1}^{o} = \frac{5139}{T} - 12.621 \tag{3.9}$$

$$\log_{10} K_{p2}^{o} = \frac{-2073}{T} + 2.029 \tag{3.10}$$

We calculated the equilibrium conversion from CO_2 to MeOH using both the literature values listed by Graaf & Winkelman (2016) and the equations provided by Graaf et al.

(1986). To find the equilibrium value for $conv.\,\%$ we used the Goal seek -function in Excel. The equilibrium conversion results obtained with our method are presented in Figure 19.

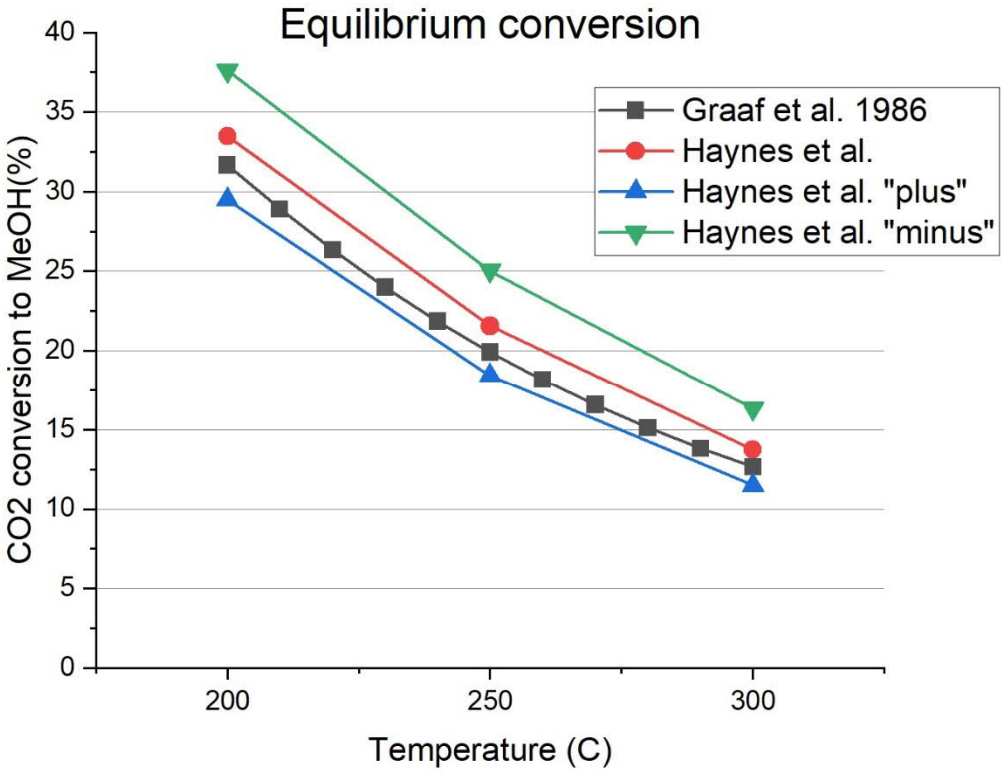


Figure 19. Equilibrium CO_2 conversion to methanol obtained with our own method of estimation. Different lines represent the equilibrium conversion obtained using K values from different sources.

These results make sense, as according to Le Chatelier's principle, the equilibrium constant K decreases for exothermic reactions and increases for endothermic reactions when temperature is increased. CO_2 hydrogenation being an exothermic reaction, the equilibrium should switch to favor reactants with increasing temperature. At the same time RWGS reaction should start to favor more the products (CO and H_2O). This means that if the temperature for methanol synthesis is increased, the equilibrium yield of methanol decreases.

A catalyst that allowed operation at lower temperatures where the equilibrium conversion is higher, without compromising the reaction kinetics would be a huge improvement for the process. If this kind of catalyst was developed, it could provide a much-needed increase of per pass conversion for methanol synthesis from CO_2 and H_2.

4 Methanol reactor setups found in literature

Methanol reactors have been studied for decades, and there are multiple studies found in literature made with either lab scale or pilot scale experimental methanol reactor setups. A literature review analyzing some of these studies is presented in this chapter. The reactor setup, equipment, catalyst, and the methanol production process conditions used in these studies are analyzed and discussed. The goal of this literature review is to develop an understanding about different aspects in constructing and operating an experimental methanol reactor setup, as well as interpreting results. This analysis considers only reactor setups that use CO_2 and H_2 as raw materials for methanol synthesis, as syngas-based or other types of reactor setups are not relevant for the topic of this thesis.

Before continuing, it is important to understand that in literature, different expressions are often used to describe the same thing. Especially expressions like CO_2 conversion, methanol yield and STY can be used to refer many different things in different publications. In this thesis, we define CO_2 conversion and methanol yield as described in Equations 4.1 and 4.2:

$$CO_2\ conversion = \frac{\dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}}{\dot{n}_{CO_2,in}} \tag{4.1}$$

$$Methanol\ yield = \frac{\dot{n}_{CH_3OH,out}}{\dot{n}_{CO_2,in}} \tag{4.2}$$

where $\dot{n}_{CO_2,in}$ is the inlet molar flowrate of CO_2 into reactor, and $\dot{n}_{CO_2,out}$ and $\dot{n}_{CH_3OH,out}$ are the outlet molar flowrates of CO_2 and methanol respectively at the reactor output. The term “equilibrium yield” is used to refer to methanol yield in the equilibrium in this chapter. STY represents the amount of methanol produced per amount of catalyst per hour. STY and GHSV can both be expressed with either gravimetric units (g, kg, etc.) or volumetric units (liter, cubic meter, etc.).

When comparing literature values to each other in this thesis, all values of GHSV are expressed in liters of feed gas per liters of catalyst per hour $\frac{L_{gas,in}}{L_{cat} \times h}$ (providing all necessary information such as the density of the catalyst is reported) and the unit is expressed as h^{-1}. The volumetric units are always in STP conditions.

4.1 Study 1: Doss et al. (2009)

Doss et al. (2009) conducted a study to demonstrate the feasibility of producing carbon neutral synthetic methanol from CO_2 and H_2 and to determine the optimal reaction conditions. They operated the reactor in different pressures and temperatures while also changing the gas hourly space velocity. The reactor output was measured gravimetrically and analyzed as a function of temperature, pressure and space velocity, to determine the optimal reaction conditions for producing methanol.

In their study, Doss et al. (2009) used a single-pass methanol system with an in-house built cylindrical fixed-bed reactor. The reactor had an internal diameter of 1 inch (2.54 cm) and a length of 12 inch (30.5 cm), giving it a volume of 0.154 liters. Compared to the experimental

reactor we constructed in this master's thesis, the reactor used by Doss et al. (2009) was around ¼ of its volume. The single-pass reactor system used by Doss et al. (2009) is described in Figure 20 below. The reactor was isothermal, meaning the temperature was maintained constant inside the reactor.

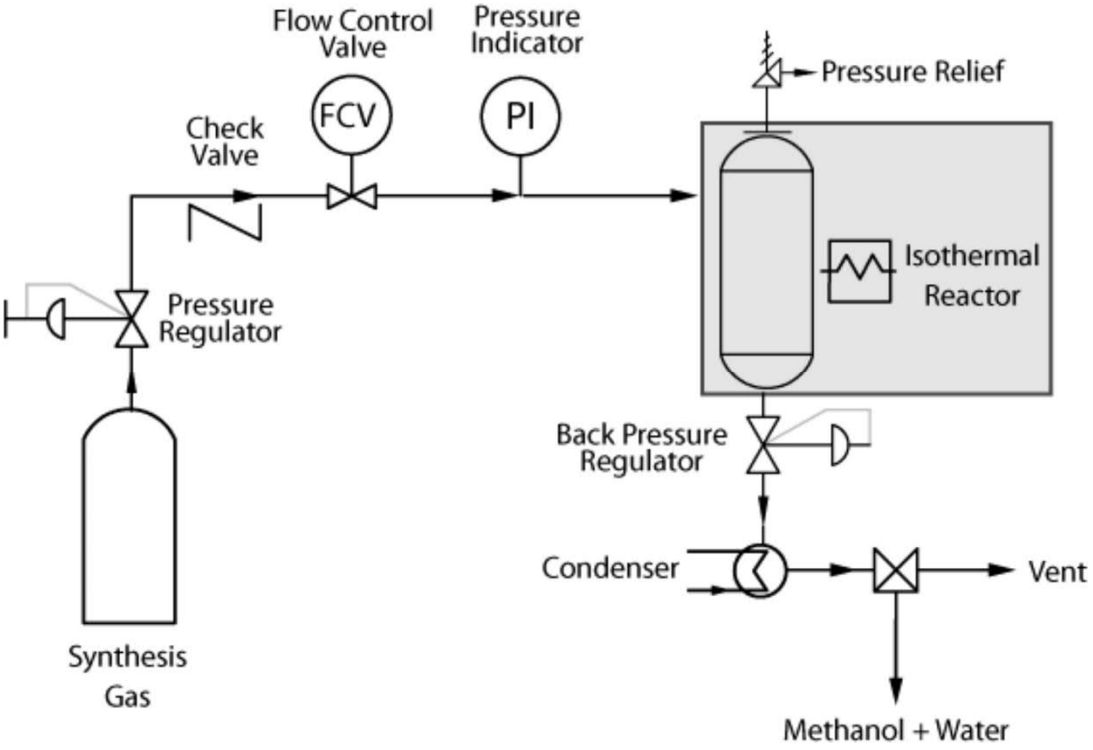


Figure 20. The reactor setup used by Doss et al. (2009).

The feed gas used by Doss et al. (2009) was premixed 75 % H_2 and 25 % CO_2. So, the composition of reaction compounds was stoichiometric. The premixed gas was received from Praxair, Inc. The flow rates were controlled with Brooks 5850 mass flow controllers, the same ones we use for controlling mass flow in our own experimental setup. A commercial catalyst, Katalco 51-8, delivered by Johnson Matthey, Inc. was used in the study. The catalyst was described in the paper as "$Cu/ZnO/Al_2O_3$ catalyst" (Doss et al., 2009: 4648). The catalyst was loaded in the reactor and used as received in solid cylindrical pellets. The pressure in the reactor was controlled with a back-pressure regulator, and the temperature was maintained constant with an external heating block and a temperature controller. The temperature inside the reactor was measured with a thermocouple positioned near the center of the catalytic bed.

Doss et al. (2009) studied the effects of temperature, pressure and gas hourly space velocity on the performance of their reactor system. They conducted two different sets of measurements, first with different temperatures and later with different space velocities and pressures. In the first measurements, they altered the reactor temperature in order to determine the optimal reaction temperature to be used in the subsequent measurements. They operated the reactor in temperatures between 220 – 260 °C in three different pressures: 1000 psi, 1200 psi and 1400 psi (68.9 bar, 82.7 bar and 96.5 bar respectively). 60 g of catalyst was loaded for this experiment, and the space velocity used was 10 000 h^{-1}. The unit Doss

et al. (2009) used for gas hourly space velocity was $\frac{L_{syngas}}{L_{catalyst} \times h}$, and in this chapter we will use the abbreviation h^{-1} to describe it.

They found that while the temperature had little effect on methanol yield in 1000 psi and 1200 psi pressures, the effect was more significant at 1400 psi. The maximum methanol yield at 1400 psi was reached at 240 °C. This temperature was then chosen as the set point for subsequent measurements. Figure 21 presents the results of their first measurement. Doss et al. (2009) defines "CO_2 conversion" as the "molar ratio of methanol produced to total CO_2 flow through reactor" (Doss et al., 2009: 4649). As described earlier, we have defined that ratio as methanol yield. Figure 21 is taken from the publication, so the y-axis is titled as defined in Doss et al. (2009).

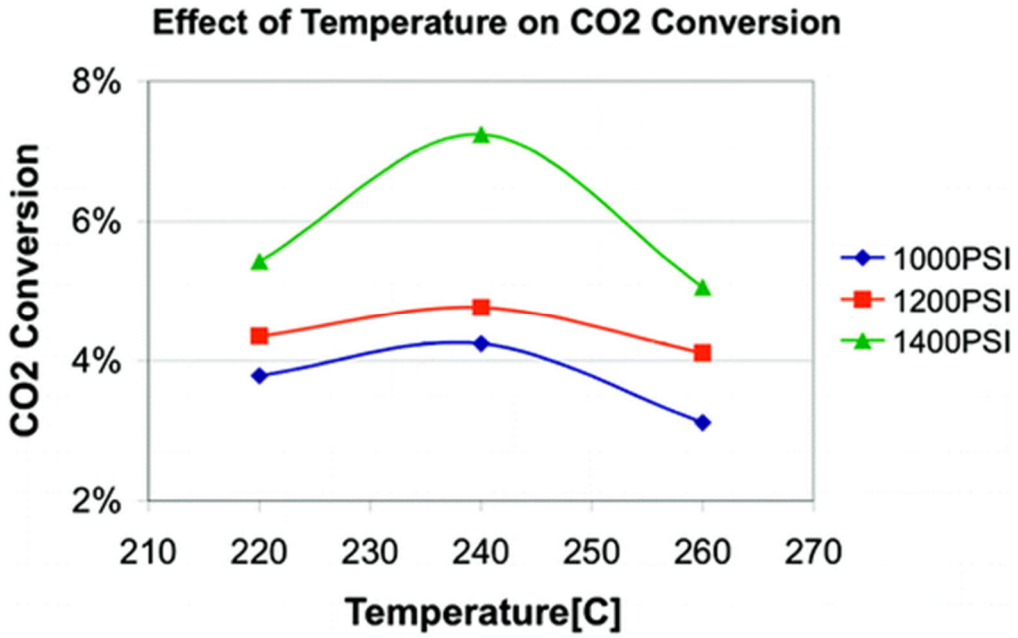


Figure 21. The effect of temperature on methanol yield presented by Doss et al. (2009).

Doss et al. (2009) then continued to run the second set of experiments where they measured the reactor performance in different pressures and with different space velocities. The temperature was set to 240 °C. The reactor was operated in pressures of 1000 psi, 1400 psi and 1800 psi (68.9 bar, 96.5 bar and 124 bar respectively). At every pressure level three different space velocities were used: 3300 h^{-1}, 5000 h^{-1} and 8300 h^{-1}.

Doss et al. (2009) used methanol yield (titled as CO_2 conversion) and space time yield to analyze the reactor performance. The results for the effect of pressure and GHSV for methanol yield and STY are presented in Figure 22 and Figure 23 respectively.

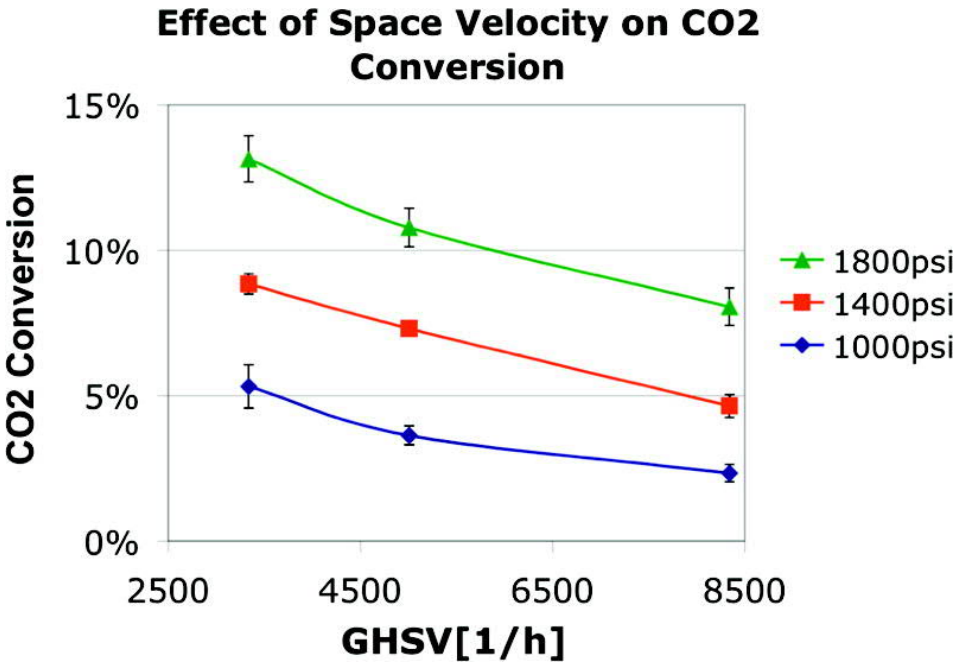


Figure 22. The effect of pressure and space velocity on methanol yield presented by Doss et al. (2009).

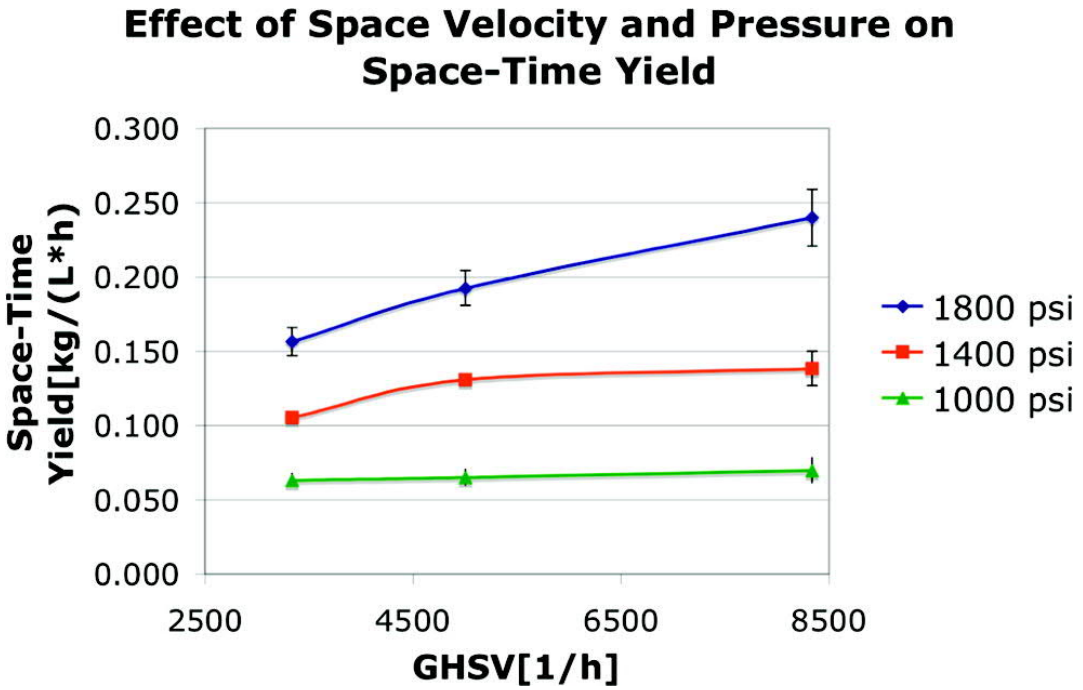


Figure 23. The effect of pressure and space velocity on space time yield presented by Doss et al. (2009).

Doss et al. (2009) analyzed the carbon monoxide concentration in the reactor exhaust stream with Fourier-transform infrared spectroscopy. They also analyzed the by-products formed in the methanol synthesis with capillary gas chromatography. The by-products were identified as ethanol, isopropanol, 1-propanol, 2-butanol, 1-butanol and 2-methyl-1-propanol, with an overall share of by-products of less than 0.05 % (volumetric) (Doss et al., 2009). These are also some by-products we can expect to find in the reaw methanol produced with our experimental setup. As pointed out by Doss et al. (2009), none of the identified by-products

should have negative impact on engine performance if used in modern vehicles. The results of the carbon monoxide (CO) analysis and by-product analysis are presented in table 4.

Table 6. The collected results of methanol synthesis experiments (Doss et al., 2009, Table 2, modified).

pressure (psi)	*GHSV (h^{-1})*	*methanol yield (mol %)*	*CO (mol %)*	*by-products (vol %)*
1000	3300	5.81 ± 0.8		
	5000	3.97 ± 0.3		
	8300	2.56 ± 0.3		
1400	3300	9.7 ± 0.4	7.9	
	5000	8.0 ± 0.2	12.7	0.017
	8300	5.1 ± 0.4		
1800	3300	14.3 ± 0.9		
	5000	11.8 ± 0.7		0.032
	8300	8.8 ± 0.7		

Doss et al. (2009) measured the molar CO concentration of the reactor output gas at 1400 psi (96.5 bar) for the GHSV of 3300 h^{-1} and 5000 h^{-1} as seen from table 4. The measured CO concentration was remarkable, even higher than the methanol yield in the GHSV = 5000 h^{-1} run, meaning that more CO_2 was converted to CO than to methanol. However, at lower space velocity (GHSV = 3300 h^{-1}) the methanol conversion was higher than the CO concentration at the reactor output. Since space velocity is directly linked to flowrate, this suggests that more of CO_2 is being converted to methanol and less to carbon monoxide with lower flowrates, and vice versa with higher flowrates. This would seem to suggest that the reverse water-gas shift reaction (reaction 2.1) is faster to reach equilibrium than the CO_2 hydrogenation reaction (reaction 2.3) as also pointed out by An et al. (2009).

Doss et al. (2009) achieved optimal methanol yield of 14.3 % at the temperature of 240 °C and the pressure of 124 bar (1800 psi) with a gas hourly space velocity of 3300 h^{-1}. However, the operating pressure of 124 bar is very high considering the limitations of the equipment. Therefore, Doss et al. (2009) suggested a more practical operating pressure of 1400 psi (96.5 bar). This pressure (with T = 240 °C and GHSV = 3300 h^{-1}) resulted in 9.7 % single-pass methanol yield as presented in table 4. However, this "more practical" operating pressure of 96.5 bar is still very high in our opinion.

Doss et al. (2009) considered their results promising for scale-up purposes. They reached higher methanol yields than other studies have reported. However, as they pointed out they also operated in higher pressures than most studies (96.5 – 124 bar) with a process that favors

high pressures, so higher results should be expected. Still, the methanol yield was 14.3 % at best. To achieve higher conversion efficiency, a gas recycling system should be implemented to the reactor setup. This was also noted by An et al. (2009).

4.2 Study 2: An et al. (2009)

An et al. (2009) studied methanol production from CO_2 and H_2 over a fibrous Cu/Zn/Al/Zr-catalyst. They investigated the effects of temperature, pressure and space velocity on methanol production. After the experimental part, they used their experimental data to obtain kinetic parameters by regression and used those to create a model to simulate the reactor performance by changing parameters in the setup.

The tests were conducted with a fixed-bed single-pass reactor. The reactor used by An et al. (2009) had a diameter of 12 mm and a height of 500 mm. The reactor they used was therefore a relatively thin tube reactor with a volume of only 0.057 liters, even smaller than that used by Doss et al. (2009). However, their operation pressures were significantly lower. They operated in temperatures between 210 – 270 °C and the pressure was altered between 20 – 50 bar.

An et al. (2009) prepared the fibrous Cu/Zn/Al/Zr-catalyst with the composition of Cu/Zn/Al/Zr being 12:6:1:1 respectively. The catalyst was packed in the middle section of the reactor. Temperature was kept uniform over the catalyst area. However, they do not mention neither the amount of the catalyst they have used nor the catalyst density.

An et al. (2009) used a 5 % H_2 / 95% N_2 gas mixture to reduce the catalyst by slowly raising the temperature to reaction temperature over 10 hours in atmospheric pressure. After this they switched to the reaction gas and raised the pressure to the reaction pressure. First samples were taken 2 hours after steady reaction conditions were established, and from there subsequent samples were taken every 30 minutes.

An et al. (2009) ran their setup with space velocities between 1 000 – 10 000 $\frac{mL_{syngas}}{g_{catalyst} \times h}$, however most of the results were presented with the GHSV of 6 000 $\frac{mL_{syngas}}{g_{catalyst} \times h}$ (The unit An et al. (2009) used for gas hourly space velocity was $\frac{mL_{syngas}}{g_{catalyst} \times h}$. Since it has both volumetric and gravimetric units, we will not use the abbreviation h^{-1} for it for clarity). Since they did not present any information of the catalyst amount used or the catalyst density, we cannot deduce the flow rate they have used. The feed gas composition was stoichiometric.

An et al. (2009) used both CO_2 conversion and methanol yield to evaluate the reactor performance. They used the exact same definitions for these two terms that we do in this master's thesis (see Eqs. 4.1 and 4.2). The effect of temperature on CO_2 conversion and methanol yield was studied by altering the reactor temperature between 210 – 270 °C in the pressure of 50 bar, with the space velocity of 6 000 $\frac{mL_{syngas}}{g_{catalyst} \times h}$. The results of these measurements are presented in Figure 24 (temperature scale is in Kelvin).

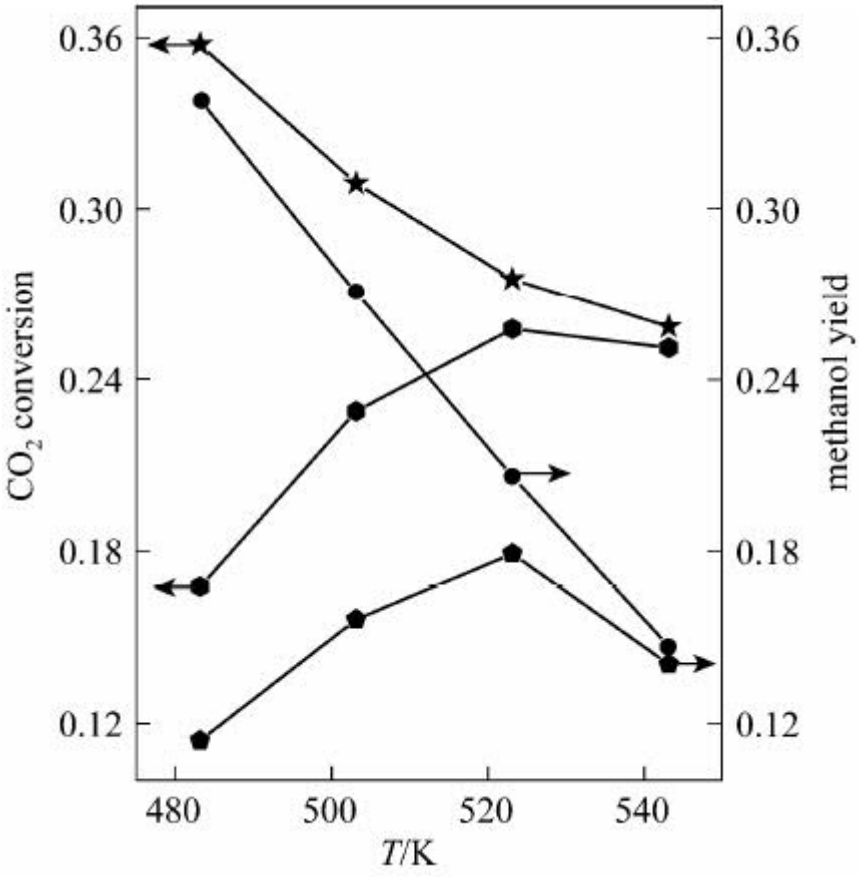


Figure 24. The experimental results of the effect of temperature on CO2 conversion and methanol yield presented by An et al. (2009). The stars present equilibrium values and the hexagons measured values for CO2 conversion. The circles present equilibrium values and the pentagons measured values for methanol yield.

An et al. (2009) compared the results from these measurements to the chemical equilibrium values (as seen in Figure 24). They found that both CO_2 conversion and methanol yield approach chemical equilibrium in increasing temperature. However, the chemical equilibrium values for CO_2 conversion and methanol yield both decrease with increasing temperature. So, there is a "sweet spot" temperature, which gives the highest CO_2 conversion and methanol yield. This temperature was 250 °C.

An et al. (2009) conducted similar measurements to study the effect of pressure on CO_2 conversion and methanol yield. The results of these measurements are presented in Figure 25. They found that both CO_2 conversion and methanol yield increased with increasing pressure. However, the equilibrium values increased even faster with increasing pressure. An et al. (2009) found that in the temperature measurements and in the pressure measurements, the CO_2 conversion was always clearly higher than the methanol yield. This is because only part of CO_2 is converted to methanol, while the rest of it is converted to CO with the reverse water-gas reaction.

The highest methanol yield achieved was 17.9 % at the temperature of 250 °C and the pressure of 50 bar with a space velocity of 6 000 $\frac{mL_{syngas}}{g_{catalyst} \times h}$. This methanol yield of 17.9 %

achieved by An et al. (2009) was a much higher compared to the 9.7 % achieved by Doss et al. (2009) even though Doss et al. (2009) conducted their experiments at 96.5 bar pressure. This could imply that new catalyst innovations, such as the fibrous catalyst used by An et al. (2009), can provide methanol yields substantially closer to equilibrium values also with higher space velocities. Developing catalysts that can help reach equilibrium at lower temperatures could help increase methanol production capacity even more.

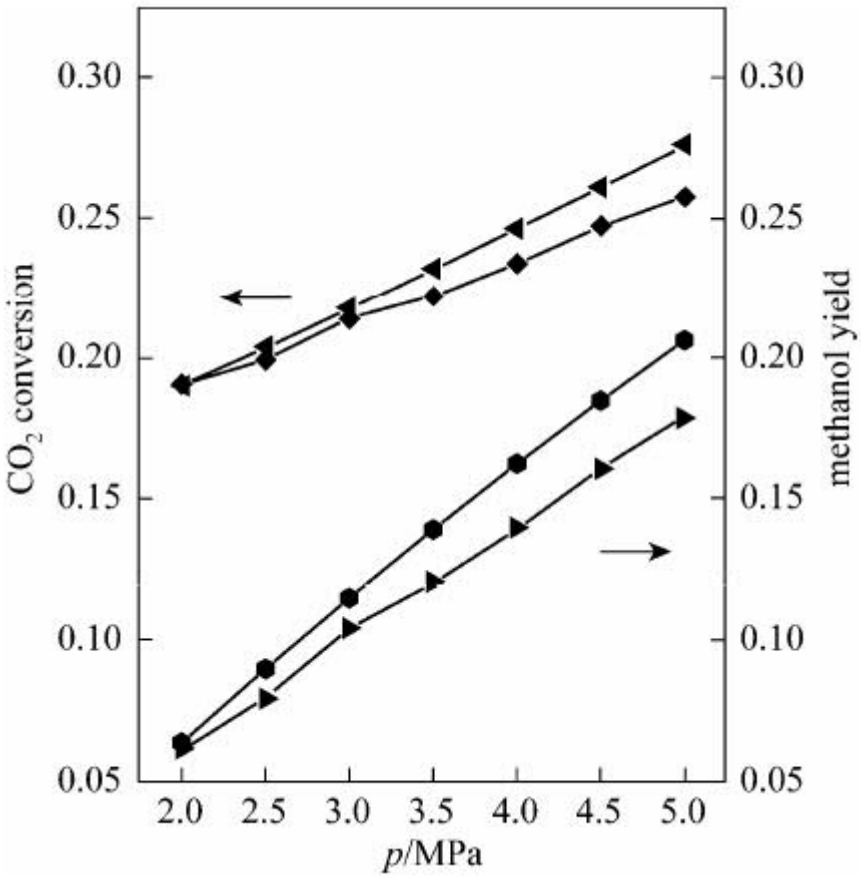


Figure 25. The experimental results of the effect of pressure on CO2 conversion and methanol yield presented by An et al. (2009). The upper triangles present equilibrium values and the squares measured values for CO2 conversion. The hexagons present equilibrium values and the lower triangles measured values for methanol yield.

Considering CO_2 conversion and methanol yield, An et al. (2009) found in their study, that the differences between experimental results and thermodynamic equilibrium increased with increasing pressure, and decreased with increasing temperature as demonstrated by Figures 24 and 25. They also found that methanol yield increased faster than CO_2 conversion when the pressure was increased. This can be explained with CO_2 hydrogenation reaction being more sensitive to pressure than the reverse water-gas shift reaction. This means that either the amount of CO_2 that is converted to CO via RWGS reaction is actually decreased with increasing pressure when CO_2 hydrogenation reaction becomes more active, or that the CO hydrogenation starts to take place as well.

An et al. (2009) studied also the effect of space velocity on methanol yield and CO_2 conversion. The results of their GHSV experiments are presented in Figure 26. Increasing

the space velocity means either increasing the flowrate in the reactor or decreasing the amount of catalyst in the reactor, or both. This results in the reactants spending less time in the reactor in touch with the catalyst, giving reactions less time to take place. Therefore, CO_2 conversion and methanol yield should both decrease, as An et al. (2009) found out was exactly what happened. However, they found that the methanol yield decreased faster than CO_2 conversion when space velocity was increased. An et al. (2009) explained this with the notion that the reverse water-gas shift reaction reaches equilibrium in a very short time. Therefore, the shorter time reactants spend in the reactor does not affect the water-gas shift reaction as much as the methanol reaction. Similar findings by Doss et al. (2009) support this idea.

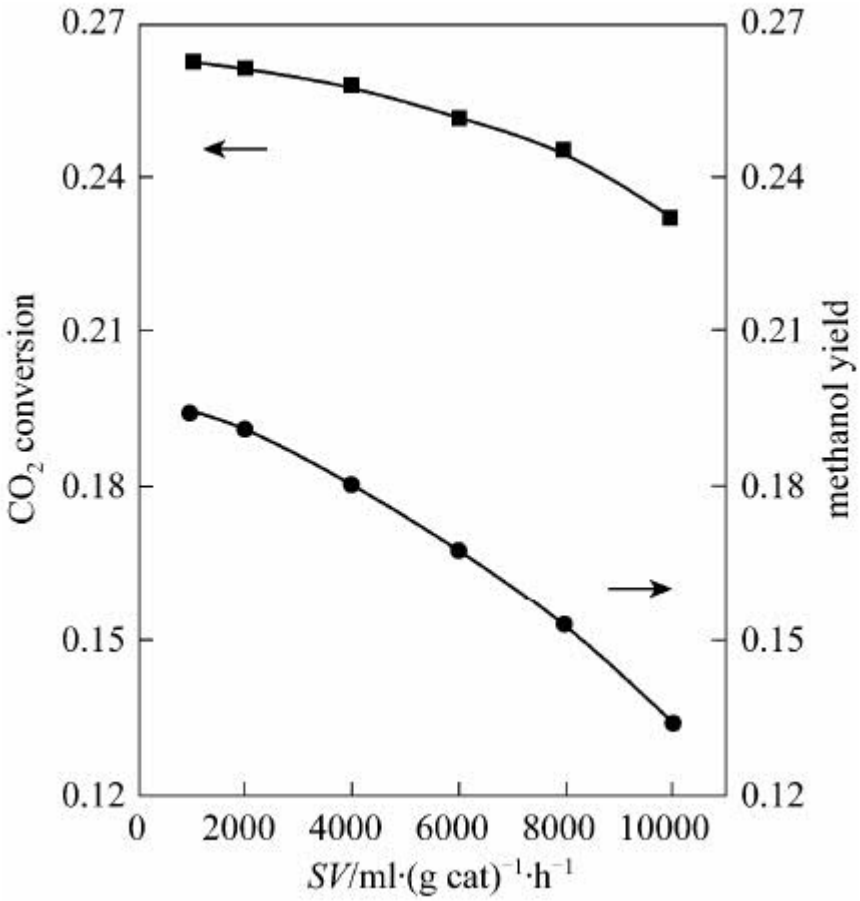


Figure 26. The experimental results of the effect of space velocity on CO2 conversion and methanol yield presented by An et al. (2009). The the squares present measured values for CO2 conversion. The circles present measured values for methanol yield.

After the experimental part, An et al. (2009) used their experimental data to create a model of the reactor system, and used their model to simulate the CO_2 hydrogenation process with an additional CO recycling in the system. We do not focus on their kinetic model or simulation in this master's thesis, as it is outside the scope of this thesis, but we wanted to present some interesting results they got using the simulation. Based on their simulation, the STY of methanol increased, and there was no CO present in the output stream. The simulation results are presented in Figure 27. This supports the impression that having a gas

recirculation in the system is needed to improve the overall efficiency of methanol production.

Table 2 Methanol yield from CO_2 hydrogenation with/without CO recycle and pressures for a stable process with CO recycle at various temperatures

T/K	*P*/MPa	Space time yield of MeOH/g·(g cat)$^{-1}$·h^{-1}	
		With recycle	Without recycle
503	2.51	0.255	0.193
513	3.07	0.303	0.237
523	3.83	0.350	0.278
533	4.78	0.389	0.313

Figure 27. The simulation results with and without CO recycling (An et al., 2009).

4.3 Study 3: Ushikoshi et al. (1998)

Ushikoshi et al. (1998) operated a test plant with a methanol production capacity of 50 kg/day. The plant was used to examine a multicomponent Cu/ZnO-based catalyst performance under "practical reaction conditions". This study is an older one from the 1990s, when a lot of catalyst compositions were studied (Bertau et al., 2014). However, it provides good experimental data of CO_2 and H_2 based methanol production on a bigger scale.

The reactor used by Ushikoshi et al. (1998) was a fixed bed reactor with a reactor tube of 4.6 liters in size (diameter: 38.4mm, length: 4m). Although Ushikoshi et al. (1998) refers to their reactor as "a small-scale reactor" in their study, compared to other experimental reactor setups found in literature, it is relatively large, being 30 times larger than the reactor used by Doss et al. (2009).

The reactor setup of Ushikoshi et al. (1998) is described in Figure 28. The reactor setup included recycling equipment for unreacted gases. The reactor output gas was cooled and the liquids (water, methanol) were condensed and separated from the gases in the gas-liquid separator. After this the unreacted gases were recycled, mixed with the feed gas, compressed and fed back the reactor. As we have discussed, the relatively low equilibrium methanol yield in the common operating conditions makes gas recycling necessary to achieve better conversion efficiencies and to save on feed gas consumption. Therefore, the gas recycling equipment was an even more essential inclusion in this experimental setup, because this reactor used by Ushikoshi et al. (1998) had significantly larger production volumes than those of An et al. (2009) and Doss et al. (2009).

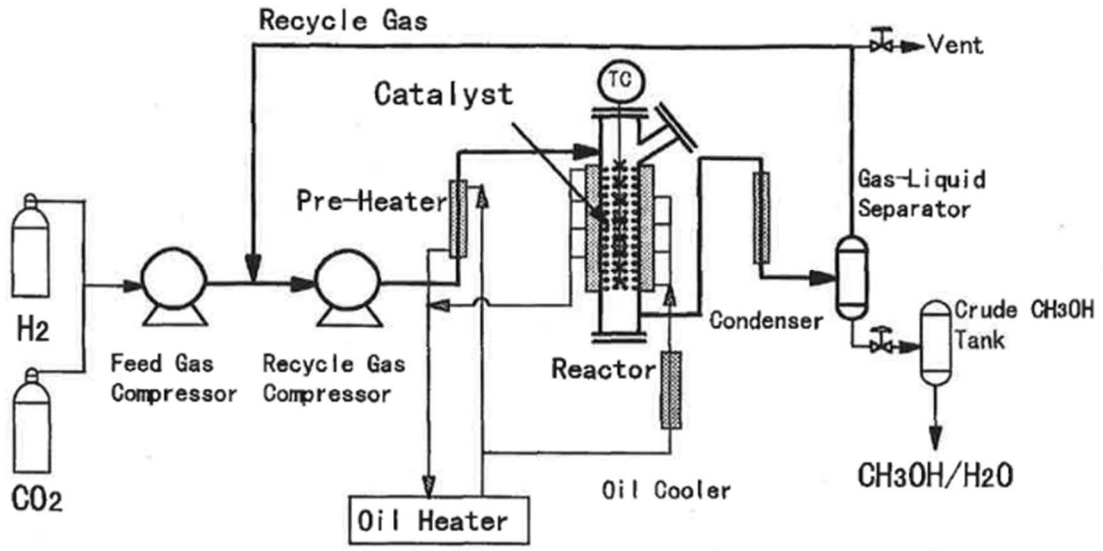


Figure 28. The experimental setup used by Ushikoshi et al. (1998).

Ushikoshi et al. (1998) used a multicomponent $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ catalyst in their experiments. The catalyst was pelletized to cylindrical samples with a diameter and height of 3 mm. Catalyst load was 3 liters for the measurements. The reactor was operated in temperatures between 230 °C – 270 °C, in total pressures between 30 bar and 70 bar and in space velocities from 5 000 h^{-1} to 20 000 h^{-1}. Feed gas composition was stoichiometric.

Ushikoshi et al. (1998) achieved a space time yield of 600 $\frac{g_{MeOH}}{L_{cat} \times h}$ (grams of methanol per liter of catalyst per hour) at 250 °C temperature, 50 bar pressure and 10 000 h^{-1} space velocity. Their results are presented in Figures 29 and 30.

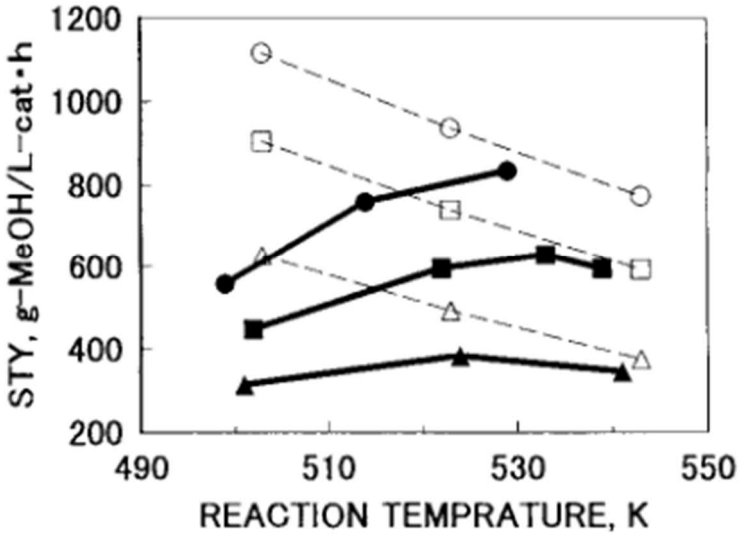


Figure 29. The experimental results for the space time yield of methanol in different temperatures and pressures from Ushikoshi et al. (1998). The circles represent values at 70 bar, the squares at 50 bar and the triangles at 30 bar. The broken lines represent values at the equilibrium, the dark lines represent experimental values. (Ushikoshi et al., 1998)

Figure 29 visualizes the behavior of the methanol synthesis very well. With increasing temperature, the equilibrium yield decreases, but the actual methanol yield gets closer to equilibrium. Both the equilibrium yield and the actual methanol yield increase with increasing pressure. Note, that even though Figure 29 plots space time yield on the y-axis instead of methanol yield, it can be used to analyze the effects of pressure and temperature on methanol yield and equilibrium yield. Changes in the STY are caused by changes in methanol yield because the space velocity and the catalyst load (and therefore flow rate) stay constant.

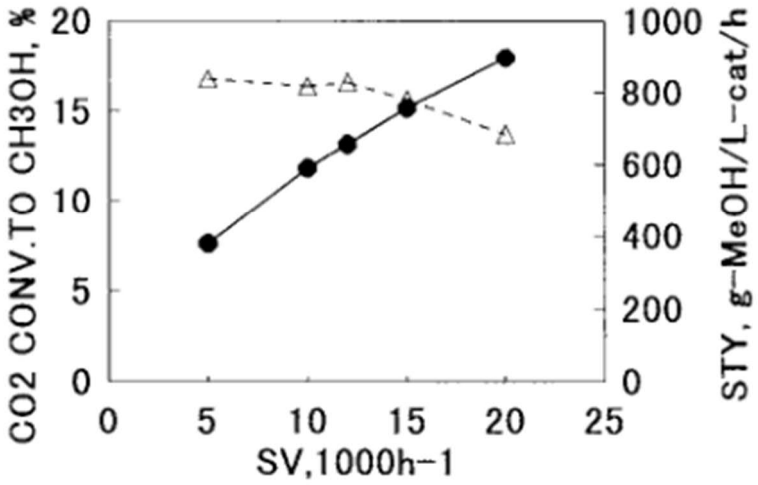


Figure 30. The experimental results for methanol yield and space time yield in different space velocities from Ushikoshi et al. (1998). The circles represent values for STY, whereas the triangles represent the values for methanol yield. (Ushikoshi et al., 1998)

Ushikoshi et al. (1998) describe methanol yield as "CO_2 conversion to methanol". For consistency in terminology, we will refer to it as methanol yield. Ushikoshi et al. (1998) did not provide exact numerical values for methanol yield, but it can be interpreted from Figure 30 to be 16 % at 250 °C and 50 bar with the space velocity of 10 000 h^{-1}.

Ushikoshi et al. (1998) also analyzed the composition of the products at the reactor outlet with gas chromatography (GC). They used a thermal conductivity detector (TCD) for the analysis of CO_2, H_2 and CO, and a flame ionization detector (FID) for the analysis of methanol, DME, methyl formate and other hydrocarbons. The working principles of GC, TCD and FID are explained in chapter 5.1. The purity of the raw methanol produced was found to be higher than 99.9 % (excluding water). The most common impurity excluding water was methyl formate. This is consistent with the findings of Doss et al. (2009). Ushikoshi et al. (1998) suggest that this level of impurities is much lower than that observed in the syngas-based methanol synthesis. Their reasoning behind this is that CO is much more reactive with H_2 than CO_2 to produce higher alcohols and other hydrocarbons. The raw methanol composition analyzed by Ushikoshi et al. (1998) is presented in Table 7.

Table 7. Raw methanol composition at different temperatures from the experiments of Ushikoshi et al. (1998)

Compound	*503 K*	*523 K*	*524 K*
Methanol	63.3 wt.%	63.0 wt.%	64.4 wt.%
Water	36.7 wt.%	36.9 wt.%	35.6 wt.%
Methyl formate	450 ppm	290 ppm	270 ppm
Ethanol	12 ppm	18 ppm	46 ppm
1-Propanol	not detected	6 ppm	8 ppm
2-Propanol	7 ppm	9 ppm	17 ppm
2-Butanol	9 ppm	12 ppm	21 ppm

4.4 Comparison of literature results

The methanol yield of 16 % achieved by Ushikoshi et al. (1998) is of similar proportions than the 17.9 % achieved by An et al. (2009). Considering Ushikoshi et al. (1998) had gas recirculation included in their setup while An et al. (2009) did not have, highlights the high methanol yield achieved by An et al. (2009). Another study that did not include gas recirculation was the study by Doss et al. (2009). However, they did not achieve as high yield as An et al. (2009) even though they operated at much higher pressures. The comparison of the results of these three studies is presented in Figure 31.

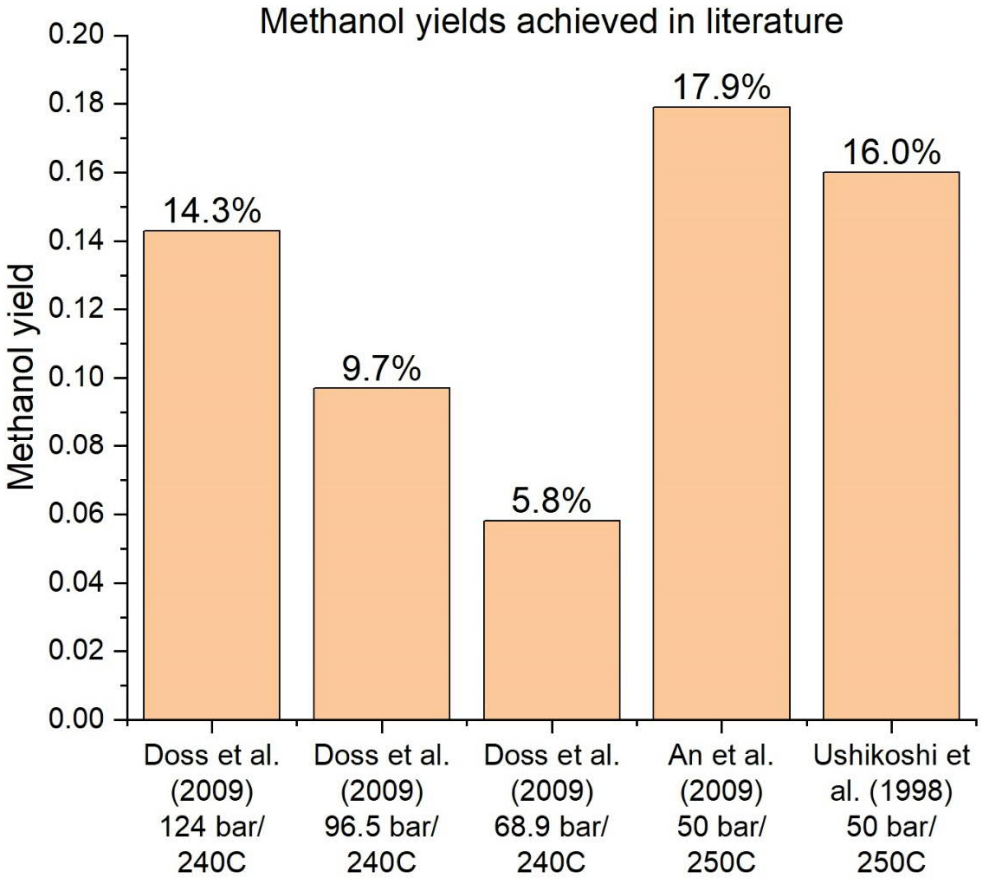


Figure 31. Comparison between the methanol yields measured in different experimental setups found in literature.

In addition to analyzing these studies, we compared them and two other studies by Portha et al. (2017) and Park et al. (2014) in terms of their reactor size, operating conditions and methanol yield. The different experimental conditions used in different literature studies is presented in Table 8. What can be seen from Table 8, is that the methanol yield results can vary greatly between different studies. Even with much higher pressures reported by Doss et al. (2009) and Portha et al. (2017), they could not achieve as high methanol yields as for example An et al. (2009) with achieved with only 50 bar pressure.

In the study of Park et al. (2014), the highest achieved methanol yield was 40.42 %. This can be explained with the way how the methanol yield is calculated, and with the fact that Park et al. (2014) used a non-stoichiometric feed gas composition in some of their runs. In the run that resulted in this extremely high methanol yield, their experimental setup was operated with a feed gas with the composition of 12 % CO_2 and 86 % H_2 (and 2 % argon). This means that there was much more H_2 than CO_2 compared to the stoichiometric ratio, which helped to push the equilibrium considerably towards the products, thus enabling such high yield. With stoichiometric feed gas composition this high conversions could not be achieved due to equilibrium limitations.

Table 8. An overview of the conditions used in different experimental reactor setups found in literature (= feed gas composition not stoichiometric).*

Study	*Reactor size (L)*	*Temperature (°C)*	*Pressure (bar)*	*GHSV (h^{-1})*	*Methanol yield (highest achieved)*
Doss et al. (2009)	0.154	220 – 260	68.9 – 96.5	3300 – 8300	14.3 %
An et al. (2009)	0.057	210 – 270	20 – 50	1 000 – 10 000	17.9 %
Ushikoshi et al. (1998)	4.6	230 – 270	30 – 70	5 000 – 20 000	16.0 %
Portha et al. (2017)	N/A, Inner diameter: 1.01 cm	200 – 230	50 – 80	7 800 – 23 400	6.0 %
Park et al. (2014)	N/A, Inner diameter: 0.7 cm	250	50 – 70	8 000	40.42 %*

5 Construction of experimental methanol reactor

Part of this thesis includes the design and construction of an experimental setup for methanol synthesis from CO_2 and H_2. The reactor setup is constructed for testing the potential of the methanol synthesis process and gathering data about its performance. With the experimental data from the results of reactor performance in different conditions, we can simulate different aspects of the reactor behavior and try to develop the system further. Possible research topics are the heat transfer in the reactor, the development of a kinetic model using the experimental results, or geometrical optimization of the reactor and the catalyst using computational fluid dynamics.

The overview of our single-pass methanol reactor setup is presented in Figure 32. The reactor setup consists of the feed gas bottles with mass flow controllers, oil-heating and water-cooling system, the single bed isothermal tube reactor, heat exchangers for feed heating and product cooling, gas-liquid separator, product tank and gas outlet, and two gas chromatographers (GC), along with piping, valves and pressure and temperature sensors. A commercial Cu/Zn/Al/Mg-catalyst is used in the reactor. The equipment is presented in more detail in chapter 5.1.

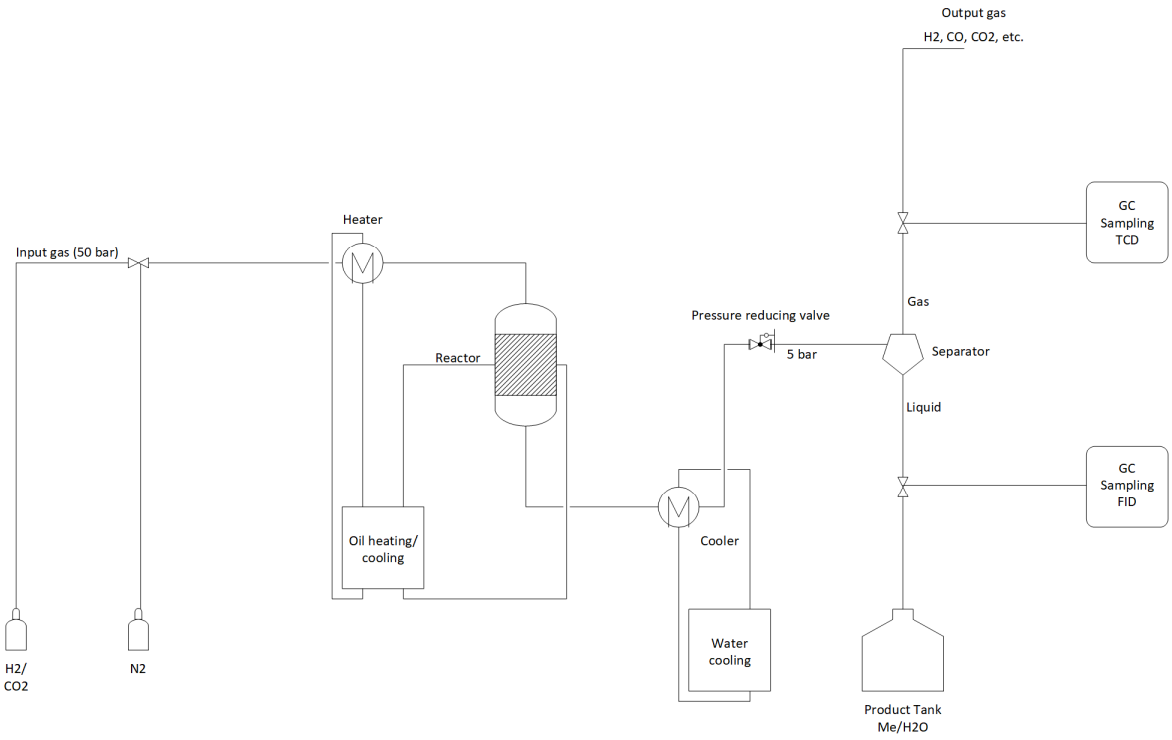


Figure 32. Our experimental single-pass reactor setup for methanol synthesis. Larger version of the figure can be found in appendix 1.

The operation of our experimental reactor can be approximately described as follows: First the pre-mixed gas mixture of CO_2 and H_2 exists the gas cylinder at 200 bar pressure at the laboratory room temperature. The gas proceeds to a heat exchanger where it is heated to circa 250 °C by the heating oil circulating on the other side of the heat exchanger. Then the gas enters the reactor at 200 bar pressure and 250 °C temperature. The gases react in the reactor on catalyst surfaces via surface reactions to produce MeOH, H_2O, CO and possibly

some other by-products. The reactor is cooled with circulating oil to keep it isothermal. After the reactor the output is cooled with another heat exchanger, this time with water instead of oil. Then the pressure is reduced to 5 bar, and the liquids are separated from the gases in the droplet separator. The pressure of the liquid products is then reduced to ambient pressure, and the crude methanol is collected to the product tank. The gases are directed out via the fume cabinet ventilation system.

Our experimental setup is designed for operation in 50 bar pressure and 230 – 250 °C temperature. Since our experimental setup does not include a gas compressor, we take the feed gas from the gas cylinders at 50 bar directly. The GHSV used in our system during operation are to be mostly below 10 000 h^{-1}, somewhere in the range of 1 000 – 5 000 h^{-1}. This is purely for the purpose of managing the feed gas consumption, as we do not have re-circulation of unreacted gases in our system. The reactor setup can also be used in different operating conditions with some limitations such as the maximum operating temperature for some of the equipment being close to 250 °C. Lower temperatures and lower pressures are easier to apply.

Operation with the experimental setup is to be started soon after the publication of this master's thesis. First tests are to verify that the experimental setup works properly and produces methanol. After ensuring stable operation, the key interests in the very first runs are the effects of temperature, pressure and GHSV on the methanol yield. The comparison of our results for methanol yield with different conditions to the equilibrium yield is one of the major points of interest. How the behavior of our experimental setup compares to that of other experimental setups such as the ones presented in chapter 4, will help us understand the possibilities and limitations of our equipment.

5.1 Equipment

Our reactor setup is a single-pass reactor setup which means that there is no re-circulation for the unreacted gases. However, the system can be later modified to include re-circulation. Our current reactor setup is presented in Figure 32, whereas the setup including the possible re-circulation is presented in Figure 36 in chapter 5.2. This sub-chapter describes the equipment used in our current reactor setup.

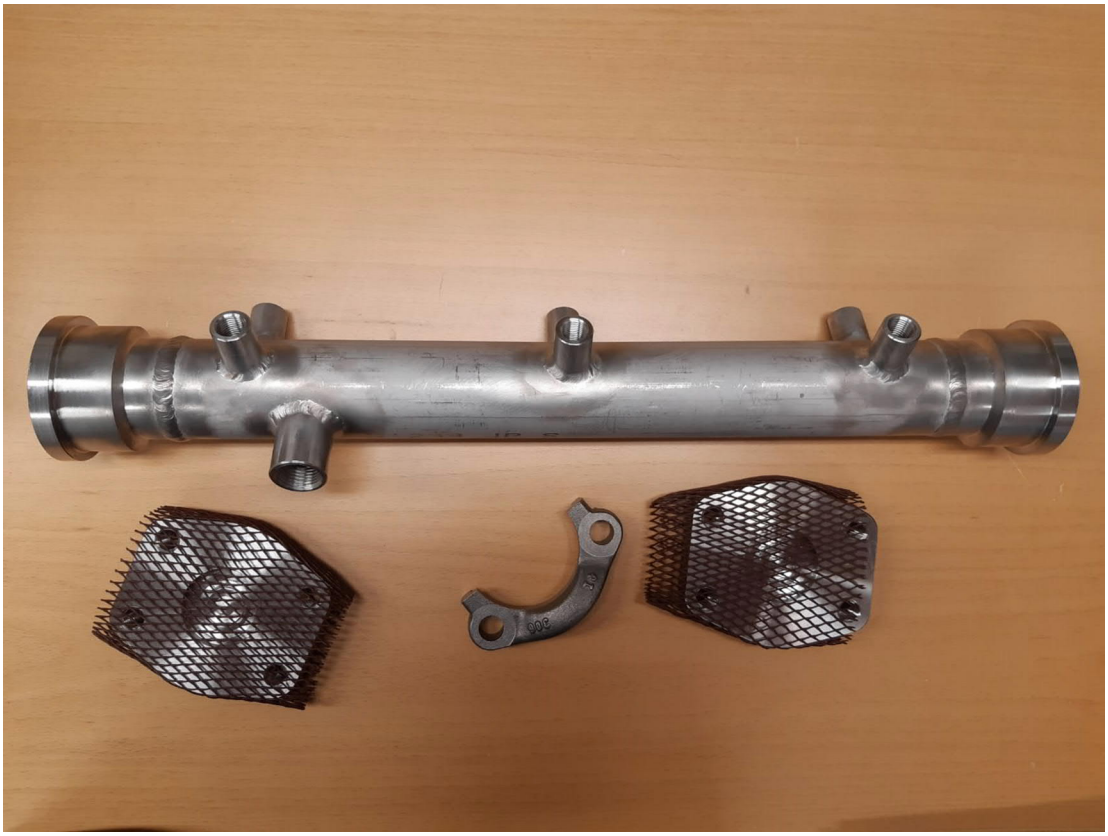


Figure 33. The in-house designed methanol reactor used in our experimental setup.

The reactor itself is a single bed isothermal tube reactor, with 50 cm height and 4.0 cm inner diameter. The volume of the reactor is approximately 0.63 liters, making our reactor an intermediate in size between the reactor used by Doss et al. (2009) and Ushikoshi et al. (1998), their reactors being 0.154 and 4.6 liters respectively. The reactor was customized in-house. Three places for pressure sensors and thermal sensors were implemented on the top, middle and bottom part of the reactor tube. The sensors are attached to the inserts to collect data from different parts of the reactor. A live picture of the reactor is presented in Figure 33, and the reactor structure is illustrated in more detail in Figure 34. The reactor temperature is controlled with oil cooling implemented into the reactor structure.

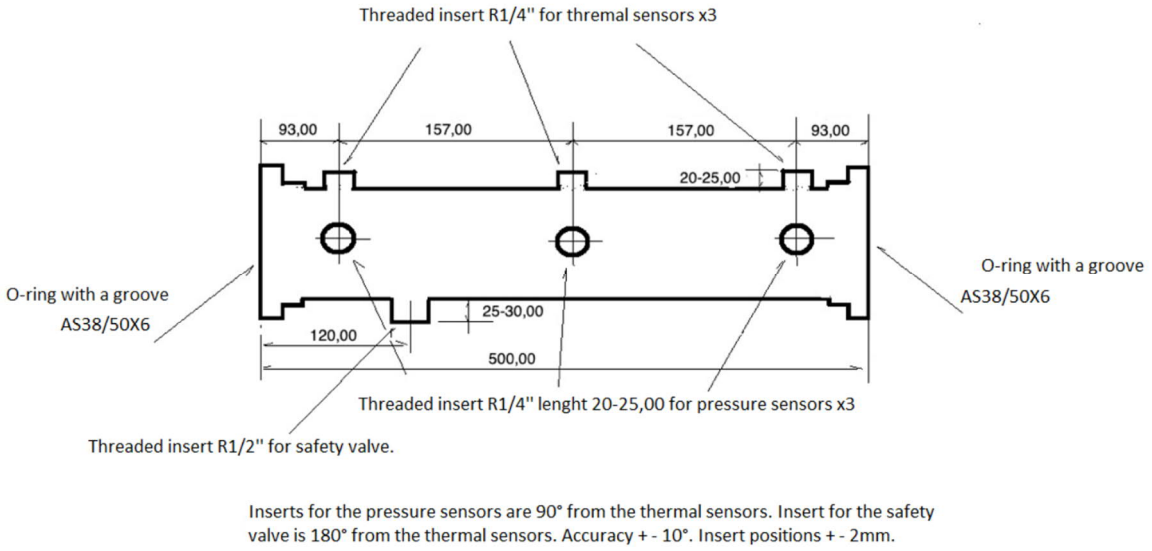


Figure 34. The dimensions of the methanol reactor used in our experimental setup.

The catalyst used in our reactor is a commercial catalyst with the following composition: Al_2O_3: 8 – 12 wt.%, CuO: 60 – 68 wt.%, MgO: 1 – 3 wt.%, ZnO: 22 – 26 wt.% (Thermo Fisher, 2020). The catalyst was delivered as 5.4 x 3.6 mm pellets and used as delivered. We mixed the catalyst pellets with silicon carbide powder, which acts as an inert material. The silicon carbide powder and the catalyst pellets are uniformly mixed in the reactor bed. First set of experiments are to be run with 100 g catalyst load.

For the feed gas, we ordered a premixed $H_2/\,CO_2$ gas cylinder from Oy Linde Gas Ab with H_2 to CO_2 ratio of 3:1 (stoichiometric ratio). Brooks 5850 mass flow controllers provided by Brooks Instrument are used to control the volumetric flowrate of the feed gas. As can be seen from Figure 32, we have also a N_2 gas cylinder included in our setup. The nitrogen gas is fed to the reactor in high temperature before operation to remove all possible impurities attached to the catalyst surfaces and to blow away all oxygen from the reactor.

After taking the feed gas at high pressure (50 bar) directly from the cylinder, we need to heat it to reactor temperatures. For that our setup includes an oil heater that uses electrical heaters to heat oil and the oil then circulates to a heat exchanger where the heat transfers to the gas and heats the gas to the desired temperature (around 250 °C). The reactor is can be both cooled and heated with the oil. Before operation, the reactor is heated to operating conditions, while during operation the oil is used to remove the heat and keep the reactor isothermal. Regular tap water is used for cooling the reactor effluent.

After the reactor outlet the product gas is cooled, and the pressure is dropped below 5 bar. Then liquid products are separated from the gases in a droplet separator. The droplet separator is an in-house built vessel with many small gas marbles inside to separate liquids from the gas. After the separator, the liquid products go through another pressure reducing valve, where the pressure is reduced to ambient pressure, and the liquids are deposited to the product tank. Samples are taken from both the gas output stream and the liquid output. The gases are then deposited out via the fume cabinet ventilation system.

Two GCs are used to analyze the reactor output. The first GC is used to analyze gaseous products. It receives the gas flow directly from the reactor system, after the droplet separator. The second GC is used to analyze the liquid products. The liquid sample is collected manually from the product tank and fed to the GC for analysis. Both GCs are the same model, TRACE 1310, from Thermo Fisher Scientific Finland (Thermo Fisher, n.d.). The GC model is presented in Figure 35 below.

Figure 35. TRACE 1310 GC used to analyze the composition of our product (Thermo Fisher, n.d.).

Gas chromatography works by conducting the gases through a thin column in which each gas takes different amount of time to pass through and reach the detector located in the end of the column. The GC used for analyzing the composition of the gaseous output from the separator uses a thermal conductivity detector (TCD) to analyze gas composition. This TCD measures changes in the thermal conductivity of the column effluent to detect different gases exiting the column. The GC used for analyzing the composition of the liquid products on the other hand uses a flame ionization detector (FID). It operates by combusting all organic compounds in a hydrogen flame, and detecting the ions formed during combustion. The FID cannot detect water, but the water level in the crude MeOH product can be determined by other means.

Pressure and temperature sensors are installed to various parts of the system. The feed gas flow, heating/cooling oil flows and the cooling water flow are adjusted based on the inputs from these sensors. LabVIEW is used as an interface between the instrumentation and control. H_2 and CO detectors with alarms are installed inside the fume cabinet. Another H_2 detector is installed in the proximity of the H_2 gas cylinder.

5.2 The reactor setup with recycling

As discussed earlier in this thesis, re-circulation of unreacted gases is critical for achieving high conversion. Operating pressures for our reactor are going to be around 50 bar, and since we do not have a compressor in our setup, the high pressure needs to be taken directly from the gas bottles. However, as the pressure drops after the reactor, we would need to compress the gas back to 50 bar when re-circulating it back to the reactor. Finding a suitable compressor able to compress a hydrogen rich gas mixture to 50 bar pressure with the volumetric flow rates that we have proved to be difficult. For this reason, we were not able to include the re-circulation to our reactor setup in the first phase of its construction. However, the reactor equipment is designed so that re-circulation can be added later.

To implement re-circulation, some additional equipment is needed for the reactor setup, such as a compressor and a mixer. The compressor would need to be able to compress the gas output mixture from the separator from 5 bar to 50 bar pressure. For mixing the recycle gas with the new feed gas (make-up gas), a mixer is needed. The mixer would probably be composed of a mixing valve with a flow control device. Our experimental reactor setup with the possible re-circulation is presented in Figure 36. Another possibility is to take the make-up gas from the gas cylinders at lower pressure (5 bar) and mix it with the recycle gas at the lower pressure. The resulting gas mixture could then be compressed to 50 bar.

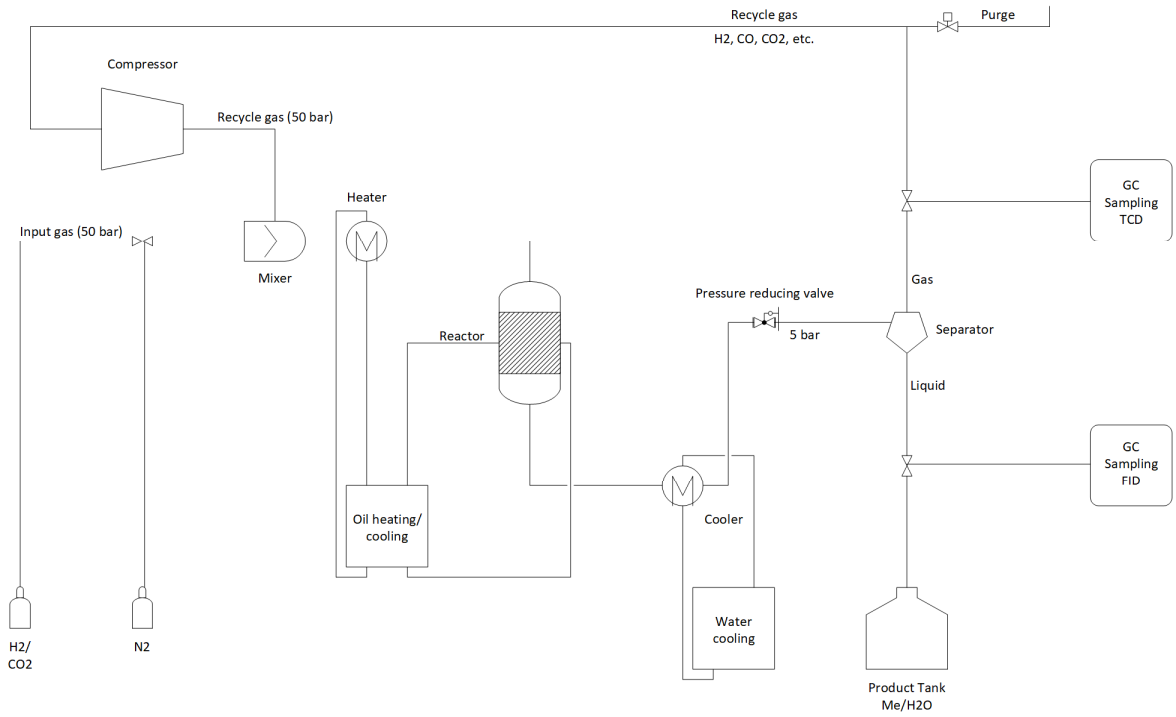


Figure 36. Our experimental reactor setup for methanol synthesis with re-circulation of unreacted gases included. Larger version of the figure can be found in appendix 2.

With the recirculation implemented in our reactor setup, the reactor could be operated with higher GHSVs. Continuous operation with GHSV between 5 000 – 20 000 h^{-1} could provide us some insight on the reaction kinetics and help us analyze the rates of the different reactions (CO_2 hydrogenation, CO hydrogenation, RWGS) in different conditions in our

reactor. Since we cannot recover the unreacted gases now, it is reasonable to first test the reactor with lower GHSV to save the feed gas.

6 Conclusions

In this master's thesis, methanol synthesis from CO_2 and H_2 was analyzed. The importance of a carbon neutral P2X process for methanol production was expressed. The behavior of methanol synthesis from CO_2 and H_2 was analyzed and discussed. Experimental studies on the subject found in literature were reviewed and their results were compared. Finally, an experimental reactor setup for methanol synthesis from CO_2 and H_2 was constructed. Here is what we found.

There are three reactions that govern methanol synthesis from carbon dioxide and hydrogen: CO_2 hydrogenation, CO hydrogenation and RWGS. These reactions usually take place in high pressures and temperatures in the presence of a catalyst. One CO_2 molecule and three H_2 molecules react to produce one MeOH molecule and one H_2O molecule.

The behavior of methanol synthesis can be explained with chemical equilibrium and reaction kinetics. Methanol synthesis favors high pressures, because CO_2 hydrogenation is accompanied with a decrease in gas moles. With temperature there is a tradeoff between chemical equilibrium and reaction kinetics. The equilibrium yield of methanol is higher with lower temperatures, but the reaction kinetics require higher temperatures to reach closer to equilibrium yield with reasonable flow rates. For this reason, a catalyst that allowed operation at lower temperatures would be a huge improvement for the process.

Compared to conventional methanol synthesis from syngas, methanol synthesis from CO_2 and H_2 is slower but more selective. This means that less by-products are formed in CO_2 -based methanol synthesis (excluding water), making the distillation process easier. This makes methanol production from CO_2 and H_2 an attractive alternative to conventional methanol production on its own. The lower per pass methanol yield in CO_2 -based methanol synthesis can be overcome by re-circulating the unreacted gases back to the reactor.

There has been an ongoing debate concerning the reaction pathway in methanol synthesis, and whether CO_2 or CO or both should be considered the primary source of methanol in methanol synthesis. This problem was analyzed in this thesis. Further analysis seems to suggest that the reaction kinetics and pathways depend on the catalyst and feed gas composition. Our experimental setup uses a stoichiometric mixture of CO_2 and H_2 for feed gas and our reactor is packed with a commercial Cu/Zn/Al/Mg -catalyst. Based on these findings, methanol can be expected to be mainly generated via CO_2 hydrogenation in an experimental setup with such specifications as ours. Depending on the kinetics of CO_2 hydrogenation and RWGS reactions, the equilibrium model created in this thesis should serve as an estimate for the highest possible single-pass methanol yield achievable.

A literature review analyzing different experimental studies of methanol synthesis from CO_2 and H_2 was conducted. The operating conditions in the analyzed studies were between 200 – 270 °C temperature and 20 – 96.5 bar pressure. The methanol yield results vary greatly between different studies. In all studies however, the trends were the same: methanol yield increased with increasing pressure and decreasing space velocity. The methanol yield approached equilibrium with increasing temperature, while the equilibrium yield decreased. So, optimal temperature could be found for maximum yield. In this thesis, that temperature

was found to be consistently around 250 °C. This behavior was present in all studies examined in the literature review.

Among the studies analyzed in the literature review, the highest methanol yield achieved with stoichiometric feed gas composition was 17.9 % at the temperature of 250 °C and the pressure of 50 bar with a space velocity of 6 000 $\frac{mL_{syngas}}{g_{catalyst} \times h}$. Our equilibrium model estimates the equilibrium yield of methanol to be between 18.4 – 25.0 % in 250 °C and 50 bar. This relatively high methanol yield was achieved with a fibrous catalyst. This might suggest that new catalyst innovations could provide methanol yields substantially closer to equilibrium values also with higher GHSVs, increasing the methanol production capacity.

However, this single-pass methanol yield of 17.9 % is not great. If the methanol yield can not be expected to exceed 20 %, the overall process becomes very inefficient. This low methanol yield could be improved with a catalyst that allowed operation at lower temperatures where the equilibrium yield is higher. The problem could also be overcome by improving the overall conversion with re-circulation of unreacted gases.

After comparing other experimental studies from the literature, an experimental setup for methanol synthesis from CO_2 and H_2 was designed and constructed. Operation with the experimental setup will start after the publication of this master's thesis. The experimental setup is to be operated in temperatures around 250 °C and in pressures around 50 bar. To achieve these conditions, the inlet gases are heated, and the reactor cooled with an oil cooling and heating system to keep the reactor isothermal. Heat exchangers are used for heating the feed gas and cooling the product. Other equipment in the setup include a gas-liquid separator for product mixture separation, valves for pressure reduction, sensors to monitor the conditions in different parts of the process, and GC for product analysis. The high pressures required for the operation are achieved by taking the gases at high pressure from the gas cylinders. However, in commercial operation with re-circulation included it would be more reasonable to include a compressor in the process.

The maximum methanol yield that can be expected from our experimental setup is around 20 % at 250 °C and 50 bar because of the limitations presented by chemical equilibrium. The by-product distribution can be expected to be similar with those found in the experiments analyzed in the literature review. Methyl formate, ethanol, 1-propanol, 2-propanol and 1-butanol are expected to be the most common by-products in the raw methanol (excluding water).

Analyzing the methanol yield, raw methanol composition, and the composition of gaseous by-products (mainly the CO formation level) with different operating conditions, can help us develop a better understanding of the CO_2 -based methanol synthesis process. When we have a better understanding of the behavior of our reactor, we can make and test hypotheses concerning methanol synthesis.

One aspect that was repeatedly expressed in literature, was the potential of re-circulation of unreacted gases in improving the overall methanol yield of the reactor. The possibility of introducing such re-circulation to our experimental setup should be considered in the future.

Adding re-circulation to the process would provide more opportunities for research and allow us to develop the methanol synthesis from CO_2 and H_2 even further.

Methanol produced from renewable sources has potential to play a major role in the shift towards clean and sustainable energy solutions, and to help climate change mitigation. However, methanol synthesis from CO_2 and H_2 has still a lot of room for improvement. Increasing the per pass conversion for methanol synthesis from CO_2 and H_2 with new catalyst innovations or by other means is a relevant topic for future research, as well as efficient re-circulation. Also, reaction pathways in the methanol synthesis process are still not completely understood. With the huge potential methanol has in P2X and CO_2 utilization, more research is needed in all possible fronts to actualize its full potential.

References

An, X., Zuo, Y., Zhang, Q., Wang, J., 2009, Methanol Synthesis from CO2 Hydrogenation with a Cu/Zn/Al/Zr Fibrous Catalyst, *Chinese Journal of Chemical Engineering*, Volume 17, Issue 1, 2009, Pages 88-94, ISSN 1004-9541, https://doi.org/10.1016/S1004-9541(09)60038-0.

Andika, R., Nandiyanto, A. B. D., Putra, Z. A., Bilad, M. R., Kim, Y., Yun, C. M., & Lee, M., 2018, *Co-electrolysis for power-to-methanol applications*, Renewable and Sustainable Energy Reviews, Volume 95, 2018, Pages 227-241, ISSN 1364-0321, https://doi.org/10.1016/j.rser.2018.07.030.

Argyrou, M. C., Christodoulides, P., & Kalogirou, S. A. (2018). *Energy storage for electricity generation and related processes: Technologies appraisal and grid scale applications*, Renewable and Sustainable Energy Reviews, 94, 804-821.

Atsonios, K., Panopoulos, K. D. & Kakaras, E. 2016, *Investigation of technical and economic aspects for methanol production through CO2 hydrogenation*, International Journal of Hydrogen Energy, Vol. 41:4. S. 2202-2214. DOI: 10.1016/j.ijhydene.2015.12.074. ISSN 0360-3199.

Bailera, M., Lisbona, P., Romeo, L. M., & Espatolero, S. (2017). *Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO2*. Renewable and Sustainable Energy Reviews, Volume 69, Pages 292-312, ISSN 1364-0321, https://doi.org/10.1016/j.rser.2016.11.130.

Bertau, M., Offermanns, H., Plass, L., Schmidt, F., & Wernicke, H. J., 2014, *Methanol: The Basic Chemical and Energy Feedstock of the Future*, Heidelberg: Springer, ISBN 978-3-642-39708-0.

Biedermann, P., Grube, T., & Höhlein, B. (2006). *Methanol as an energy carrier*. Jülich: Forschungszentrum, Zentralbibliothek.

Bozzano, G., Manenti, F., (2016) Efficient methanol synthesis: Perspectives, technologies and optimization strategies, Progress in Energy and Combustion Science, Volume 56, 2016, Pages 71-105, ISSN 0360-1285, https://doi.org/10.1016/j.pecs.2016.06.001.

Chinchen, G. C., Denny, P. J., Parker, D. G., Spencer, M. S., & Whan, D. A., (1987), *Mechanism of methanol synthesis from CO2/CO/H2 mixtures over copper/zinc oxide/alumina catalysts: use of14C-labelled reactants*. Applied Catalysis, 30(2), 333-338.

Dagdougui, H., Sacile, R., Bersani, C., Ouammi, A., (2018), *Chapter 4 - Hydrogen Storage and Distribution: Implementation Scenarios*, Editor(s): Dagdougui, H., Sacile, R., Bersani, C., Ouammi, A., *Hydrogen Infrastructure for Energy Applications*, Academic Press, 2018, Pages 37-52, ISBN 9780128120361, https://doi.org/10.1016/B978-0-12-812036-1.00004-4.

Dalena, F., Senatore, A., Marino, A., Gordano, A., Basile, M. & Basile, A., 2018, *Methanol Production and Applications: An Overview*, London, United Kingdom: Elsevier Publishing, 674 p. ISBN 978-0-444-63903-5.

Doss, B., Ramos, C., Atkins, S. (2009). *Optimization of Methanol Synthesis from Carbon Dioxide and Hydrogen: Demonstration of a Pilot-Scale Carbon-Neutral Synthetic Fuels Process*, Energy & Fuels – Energy Fuels 2009, 23, 9, Pages 4647-4650, https://doi.org/10.1021/ef900466u.

EIA, (2020), *Use of energy explained: Energy use for transportation*, U.S. Energy Information Administration [online] Available at: https://www.eia.gov/energyexplained/use-of-energy/transportation.php, [Accessed 8.7.2020].

Engineering ToolBox, (2003a), *Fuels - Higher and Lower Calorific Values*, [online] Available at: https://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html, [Accessed 8.11.2019].

Engineering ToolBox, (2003b). *Gross and Net Heating Values for some common Gases*, [online] Available at: https://www.engineeringtoolbox.com/gross-net-heating-values-d_420.html, [Accessed: 8.11.2019].

Engineering ToolBox, (2009), *Molecular Weight - Common Substances*, [online] Available at: https://www.engineeringtoolbox.com/molecular-weight-gas-vapor-d_1156.html, [Accessed: 7.5.2020].

European Commission, (n.d.a), *Paris Agreement*, European Commission, [online] Available at: https://ec.europa.eu/clima/policies/international/negotiations/paris_en, [Accessed: 2.12.2019].

European Commission, (n.d.b), *2030 climate & energy framework*, European Commission, [online] Available at: https://ec.europa.eu/clima/policies/strategies/2030_en, [Accessed: 2.12.2019].

European Commission, (n.d.c), *2050 long-term strategy*, European Commission, [online] Available at: https://ec.europa.eu/clima/policies/strategies/2050_en, [Accessed: 2.12.2019].

Graaf, G.H., Sijtsema, P.J.J.M., Stamhuis, E.J., Joosten, G.E.H. (1986), *Chemical equilibria in methanol synthesis*, Chemical Engineering Science, Volume 41, Issue 11, 1986, Pages 2883-2890, ISSN 0009-2509, https://doi.org/10.1016/0009-2509(86)80019-7.

Graaf, G.H., Stamhuis, E.J., Beenackers, A.A.C.M. (1988), *Kinetics of low-pressure methanol synthesis, Chemical Engineering Science*, Volume 43, Issue 12, 1988, Pages 3185-3195, ISSN 0009-2509, https://doi.org/10.1016/0009-2509(88)85127-3.

Graaf, G. H., & Winkelman, J. G. (2016). *Chemical equilibria in methanol synthesis including the water–gas shift reaction: a critical reassessment.* Industrial & Engineering Chemistry Research, 55(20), 5854-5864, DOI: 10.1021/acs.iecr.6b00815.

Grabow, L. C., & Mavrikakis, M. (2011). *Mechanism of methanol synthesis on Cu through CO2 and CO hydrogenation*. Acs Catalysis, 1(4), 365-384. https://doi.org/10.1021/cs200055d.

IEA, 2004, World Energy Outlook 2004, OECD Publishing, Paris, Chapter 3, pages 81-127, https://doi.org/10.1787/weo-2004-en, ISBN 92-64-1081-73-2004.

IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.

Lehtonen, A. 2019. *Kriittinen näkökulma hiilidioksidin raaka-ainekäyttöönmetanolin valmistuksessa*, Master's thesis, Aalto University, Helsinki.

Lim, H.-W., Park, M.-J., Kang, S.-H., Chae, H.-J., Bae, J. W., Jun, K.-W. (2009), *Modeling of the Kinetics for Methanol Synthesis using Cu/ZnO/Al 2 O 3 /ZrO 2 Catalyst: Influence of Carbon Dioxide during Hydrogenation*, Industrial & Engineering Chemistry Research – Ind. Eng. Chem. Res. 2009, 48, 10448-10455, doi: 10.1021/ie901081f.

Methanol Institute, n.d., *The Methanol Industry*, [online] Available at: https://www.methanol.org/the-methanol-industry/, [Accessed: 29.4.2020].

Methanol Market Services Asia, n.d., *Methanol*, [online] Available at: https://www.methanolmsa.com/methanol/, [Accessed 12.5.2020].

Mindat, (n.d.), Graphite, [online] Available at: https://www.mindat.org/min-1740.html, [Accessed: 22.11.2019].

Mitsui Chemicals, n.d., *Mitsui Chemicals to Establish a Pilot Facility to Study a Methanol Synthesis Process from CO2*, [online] Available at: https://jp.mitsuichemicals.com/en/release/2008/080825e.htm, [Accessed 25.5.2020].

Ott, J., Gronemann, V., Pontzen, F., Fiedler, E., Grossmann, G., Kersebohm, D.B., Weiss, G. and Witte, C., (2000), *Methanol*, Ullmann's Encyclopedia of Industrial Chemistry.

Park, N., Park, M. J., Lee, Y. J., Ha, K. S., & Jun, K. W., (2014), *Kinetic modeling of methanol synthesis over commercial catalysts based on three-site adsorption*. Fuel processing technology, Volume 125, pages 139-147, ISSN 0378-3820, https://doi.org/10.1016/j.fuproc.2014.03.041.

Pontzen, F., Liebner, W., Gronemann, V., Rothaemel, M., & Ahlers, B. (2011). *CO2-based methanol and DME–Efficient technologies for industrial scale production*. Catalysis Today, 171(1), 242-250.

Portha, J.F., Parkhomenko, K., Kobl, K., Roger, A.C., Arab, S., Commenge, J.M. and Falk, L., 2017. Kinetics of Methanol Synthesis from Carbon Dioxide Hydrogenation over Copper–Zinc Oxide Catalysts. *Industrial & Engineering Chemistry Research, 56*(45), pp.13133-13145.

Studt, F., Behrens, M., Kunkes, E.L., Thomas, N., Zander, S., Tarasov, A., Schumann, J., Frei, E., Varley, J.B., Abild-Pedersen, F. and Nørskov, J.K., (2015). The mechanism of CO and CO2 hydrogenation to methanol over Cu-based catalysts. ChemCatChem, 7(7), 1105-1111.

Thermo Fisher, (2020), *Copper based methanol synthesis catalyst*, Product specification, [online] Available at: https://alfaaesar.com/en/prodspec/045776, [Accessed: 10.6.2020].

Thermo Fisher, n.d., *TRACE™ 1310 Gas Chromatograph*, [online] Available at: https://www.thermofisher.com/order/catalog/product/14800302#/14800302, [Accessed: 8.7.2020].

Thiruvenkatachari, R., Su, S., An, H., & Yu, X. X., (2009), *Post combustion CO2 capture by carbon fibre monolithic adsorbents*, Progress in Energy and Combustion Science, Volume 35, Issue 5, Pages 438-455, ISSN 0360-1285, https://doi.org/10.1016/j.pecs.2009.05.003.

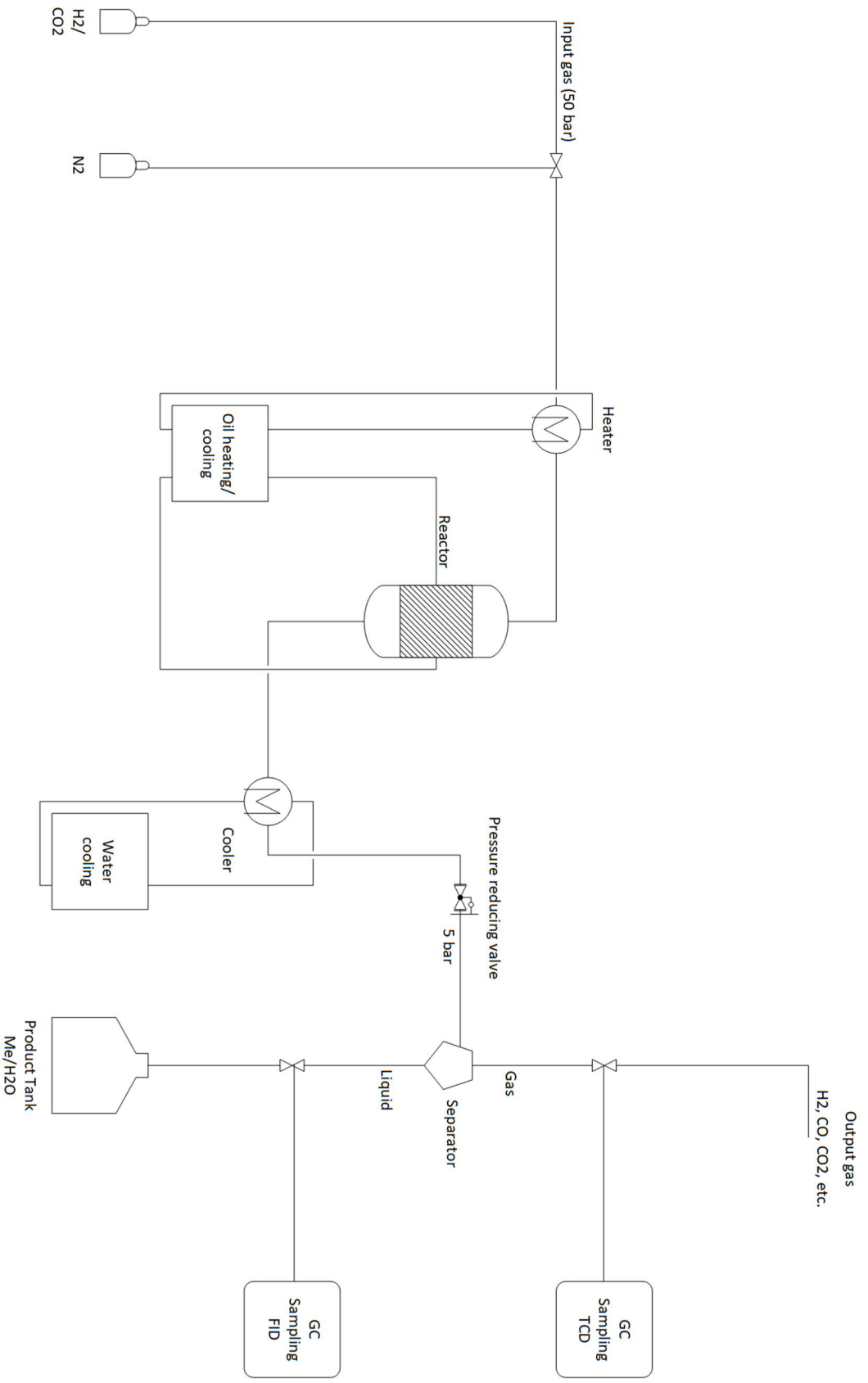
U.S. Department of Energy, n.d., *Hydrogen Storage*, U.S. Department of Energy, [online], Available at: https://www.energy.gov/eere/fuelcells/hydrogen-storage, [Accessed: 2.12.2019].

Ushikoshi, K., Moria, K., Watanabe, T., Takeuchi, M., Saito, M. (1998), *A 50 kg/day class test plant for methanol synthesis from CO2 and H2*, Editors: Inui, T., Anpo, M., Izui, K., Yanagida, S., Yamaguchi, T., Studies in Surface Science and Catalysis, Elsevier, Volume 114, 1998, Pages 357-362, ISSN 0167-2991, ISBN 9780444825742, https://doi.org/10.1016/S0167-2991(98)80770-2.

Vázquez, F. V., Koponen, J., Ruuskanen, V., Bajamundi, C., Kosonen, A., Simell, P., Ahola, J., Frilund, C., Elfving, J., Reinikainen, M., Heikkinen, N., Kauppinen, J., Piermartini, P., (2018). Power-to-X technology using renewable electricity and carbon dioxide from ambient air: SOLETAIR proof-of-concept and improved process concept, Journal of CO2 Utilization, Volume 28, Pages 235-246, ISSN 2212-9820, https://doi.org/10.1016/j.jcou.2018.09.026.

List of appendixes

Appendix 1. The single-pass experimental reactor setup



Appendix 2. The experimental setup with re-circulation of unreacted gases